Catalysis for Renewable Sources: fuel, energy, chemicals

Adriatic Riviera, Gabicce Mare, Italy
September 4-8, 2017

Fourth International Conference
CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS
CRS-4

ABSTRACTS

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ABSTRACTS

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Сборник тезисов докладов

Сборник включает тезисы пленарных, ключевых лекций, устных и стендовых докладов секций:

I. ***Catalysis in dendrochemistry for valuables production***
- Catalytic systems for hemicellulose depolymerization
- Catalytic processing of tall oil and tar, Selective conversion of sugars Catalytic transformations of CO_2 to fine chemicals

II. ***Biomass derivatives in petrochemistry***
- Catalyst application for clean syn-gas and clean hydrogen production
- Lipids in petrochemical synthesis
- Co-processing of biomass derivatives and oil feedstock

III. ***Catalytic processes for biofuels production***
- Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions
- Catalytic approaches for the processing of pyrolysis biomass products
- Conversion of carbon rich unconventional fossil resources and biomass feedstock into biofuel

IV. ***Bio-Photo-/Electro-catalytic conversion of renewables***
- Bio-catalysis for chemicals production
- Photo-catalytic for environmental protection
- Electro-catalytic conversion of renewables

V. ***Catalysis for Environment and Sustainability***
- Catalytic processes for energy efficiency and ecology
- Catalytic processing of waste

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PLENARY LECTURES

EXAMPLES OF CATALYTIC SYSTEMS ABLE TO BE APPLIED IN BIOREFINERIES

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Nowadays the society is very reliant of oil, a non-renewable raw material, used as fuels and daily chemical inputs, such as plastics. This class of materials has been widely used to replace wood, metals and even concrete. However, the world goes through a time of increase on demand for energy sources and materials, associated to an increase in ecological perception and the depletion of oil reserves that are easy to extract. In this scenario, the use of renewable inputs, which can at least partially replace fuels and raw materials of fossil origin (oil, coal and natural gas), lead to a rapid advance in research intended at the development of clean technologies, as well as the search for alternative renewable fuels, such as biodiesel. In this scenario, the obtention of industrial chemical supplies from renewable sources is a challenge that involves concepts of green chemistry and sustainability[1,2] and oleochemistry and conversion of celullose derivatives play an important role. Several catalytic systems, based on Lewis acid species, can convert renewable raw materials by important routes[3-5] and, in this presentation, some examples will be discussed.

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CAPES, CNPq, FINEP, FAPEAL, INCT-Catálise

PL-2

CHEMISTRY OF BIOMASS: NOVEL CATALYTIC DEPOLYMERIZATION PROCESSES, NOVEL BIOFUELS, NOVEL BIOPLASTICS

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Development of technological processes of mastering the renewable raw materials and energy sources requires the creation of fundamentally new knowledge on biomass chemistry. The current trend "from hydrocarbons to carbohydrates" is based on the chemical transformation of complex biomacromolecular mixtures to produce novel functionalized products.

Oxidation catalytic depolymerization of biomass. The limiting step of most biomass utilization processes is a depolymerization process to transfer oligomers and monomers in solution. Along with the improved process of enzymatic hydrolysis with participation of cellulases and xylonases, we have developed a completely novel process - the oxidation catalytic depolymerization. The features and conditions of the reaction, the catalysts and reaction products are discussed.

Biogasoline through methanogenesis. Oxidative depolymerization of biomass significantly simplifies and accelerates the process of conversion of biomass into methane under the action of anaerobic methane-generating association. The mechanism of methanogenesis, a mathematical model of the process and the transfer of methanogenesis into the mode producing the fatty acids and ethanol are discussed. Reaction products of aliphatic acids (C2-C6) with ethanol is a new automotive fuel "biogasoline". The conditions for the esterification process, catalysts and fuel characteristics are discussed.

Bioketals are the new biofuels that increase the octane number of gasoline and phase stability. Chemical modification and hydrophobization (water-repellency) of polyols, sugars and polysaccharides makes it possible to obtain products with new functional properties. We have developed a process for producing bioketals via condensation of polyols (carbohydrates) with ketones to give hydrophobized products soluble in hydrocarbon fuels. We demonstated the possibility to use them as anti-knock agents that increase the octane number of gasoline (up to 19 units), as well as the phase stable blends: gasoline - water (up to - 40 degrees).

Specific examples discussed the possibilities and features of the production of novel polymers from renewable raw materials. The driving force behind the development of new plastic is a huge accumulation of plastic waste in the form of solid waste, which is practically not utilized and do not decompose in nature. Several new polymers obtained by conversion of renewable biosubstances were described.

Biopoliesters. The pilot version was described and technologically implemented for the functionalization process of cellulosics materials via the oxidizing catalytic limited depolymerization of biomass to produce oligodicarbonic acids - the raw material for the synthesis of biopoliesters. When used as alcohol components of cellulose, hemicelluloses, polyvinyl alcohol, silicates we obtained a large set of bioplastics with various physico-chemical and physical characteristics. Specific products form new polymeric materials were demonstrated.

Biopoliamides. We have studied a polymerization process of natural amino acids via polycondensation at elevated temperatures. We also conducted kinetic and mechanistic studies of solid-phase polymerization as well as the optimal conditions for producing the polymeric materials. The samples of polyaspartic acid (polysuccinimide), polylysine, polyphenylalanine, some copolymers. The technique has been developed for amino acid polycondensation in the microwave field and a high-performance set-up has been created. A method has been developed for applying the polymer layers on the nanoparticles.

Some materials were used as the polymer electrolyte in the high capacity supercondensator.

Bacterial cellulose. A method has been developed to produce cellulose synthesized by microbial cells. As catalyst the immobilized cells were used. Synthesis of the polymer chain is carried out by bacterial enzymes, thus a nonwoven polymeric material appears with a uniform thickness of the polymer threads (filaments, fibers).

Bioplast elastomers. We have shown a possibility to obtain a natural rubber by cultivation of rubber-yielding plants in aeroponic power mode. Likewise we have shown a possibility for the beyond-soil-cultivation of kok-sagyz and the related rubber-bearing plants that may results in a continuous extraction of rubber latex.

These examples illustrate the opportunities to produce a new generation of polymeric ekomaterials using renewable sources of raw materials and new technological approaches.

PL-3

VALORIZATION OF SOLID BIOMASS RESIDUES (LIGNINS AND HUMINS) USING CATALYTIC APPROACHES

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Biorefining of lignocellulosic biomass to biofuels and biobased chemicals is receiving high attention at the moment. Most of the conversions involve the use of the sugar fraction, leaving large quantities of the lignin fraction behind. In addition valorization of the sugar fraction inevitably leads to the formation of solid byproducts known as hydrochars or humins. Both lignins [1] and humins [2] are polydisperse, highly cross linked materials (Figure 1). The valorization of these byproducts is still in a state of infancy, though is highly relevant to improve the economic attractiveness of biorefineries.

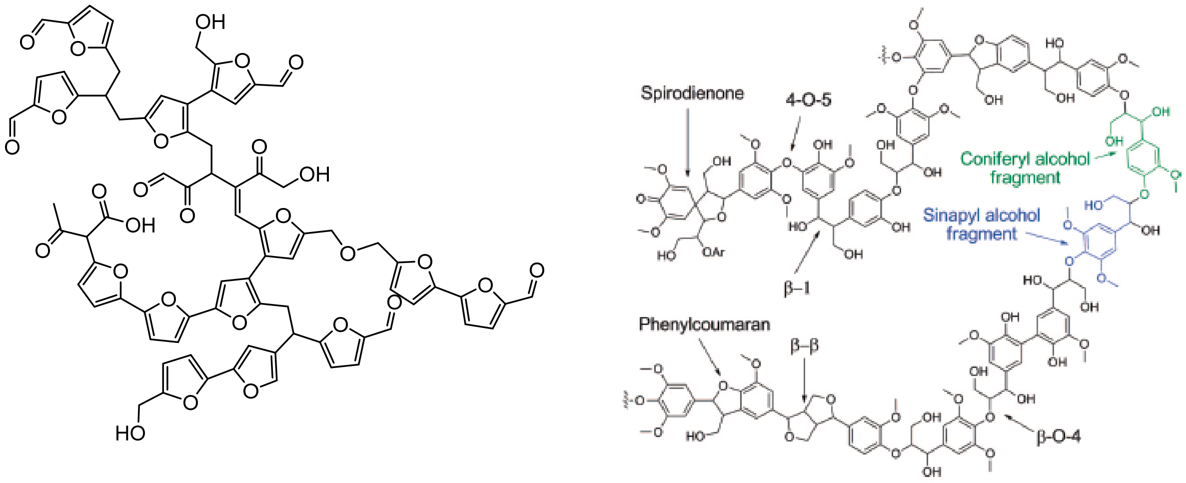

Figure 1. Proposed structure for humins from D-glucose (left) [2] and a typical lignin (right) [1]

In this presentation, recent findings on the liquefaction/depolymerisation of both lignins and humins to will be reported, with an emphasis on catalytic hydrotreatment reactions and catalytic pyrolysis [3, 4]. The product yields and compositions were determined in detail using a wide range of analytical techniques (Figure 2).

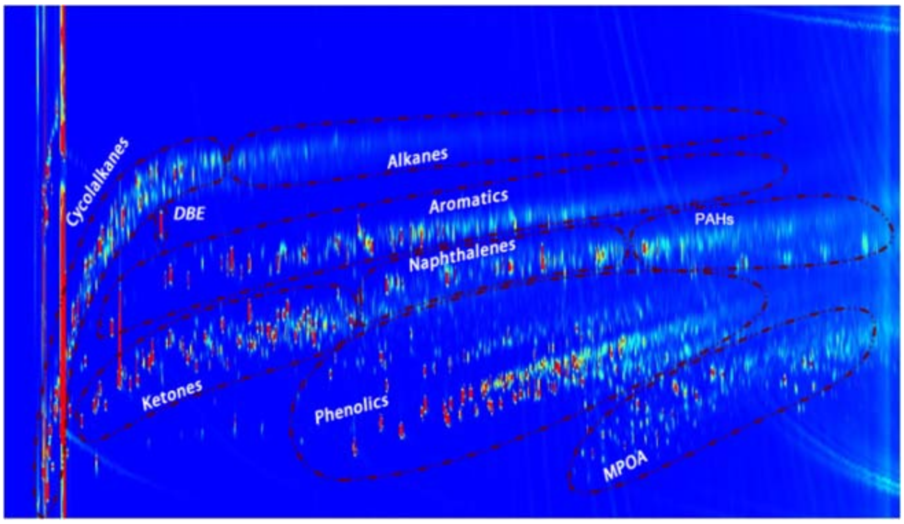

Figure 2. Representative GCxGC chromatogram of a humin oil after a catalytic hydrotreatment [3]

Reaction networks to rationalise the product portfolio were developed and will be discussed in detail.

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PL-4

UNCONVENTIONAL CATALYTIC ROUTES FOR THE VALORISATION OF BIOMASS USING LIGHT AND MICROWAVES

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The chemistry and processes involved in transforming biomass offer many challenges that continuously tantalise scientists in the search of more efficient and creative ways to minimising the energy required and overall environmental footprint. We have seen the consolidation of biotechnology as a fundamental tool in biomass transformations, particularly due to the mild conditions typically required by enzymes and microorganisms. Thermochemical transformation technologies offer many advantages over biotransformations, however, the high energetic requirements is still a draw-back. The utilisation of alternative energy vectors and *stimuli* to transform biomass, such as in the utilisation of microwave technology, sonochemistry or mechanochemistry offer some promise. However, could we possibly carry out demanding biomass transformations at very mild conditions without microorganisms or enzymes? Can the utilisation of catalysis in microwave reactors be a revolutionary tool within the biorefinery toolbox?

FUELS AND CHEMICALS PRODUCTION FROM BIOMASS: SOME SCIENTIFIC CHALLENGES FOR ACCELERATING INNOVATION AND PROCESS DEVELOPMENT

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Process development is a complex process that starts with an analysis of the technical and economic feasibilities of innovative proposals emerging from research work and ends with the oil-in of the first industrial unit.

IFPEN’s process development methodology differs significantly from the methodologies found in the available literature [1]. The key point is the pre-development phase, which makes it possible to select the best technologies and process schemes for a cost-effective, reliable process with the smallest possible ecological footprint. This is completed at a very early stage in the overall development process and at a moderate risk and cost. This initial phase uses a rigorous scientific approach to obtain the decision-making elements required to validate whether or not the initial concept is viable and to move on to the development phase of the existing process.The pre-development phase of a process identifies the key points and any relevant scientific and technological barriers that need to be removed for the subsequent development of the process.

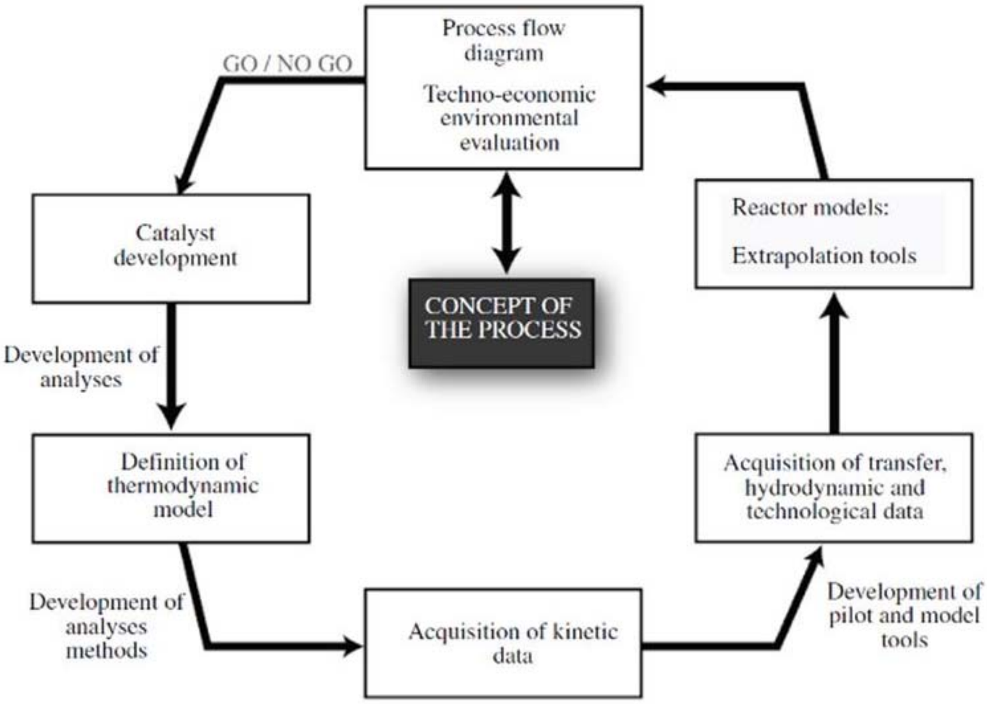
The main objective of the development phase is to determine the basic data required for industrialization: catalysts, reactor models, design criteria, optimized process flow diagrams. This phase is executed around the technological barriers identified during the preliminary studies carried out in the pre-development phase. As the research progresses on these critical points, the engineers update the technical and economic studies and redirect them if required.

Catalyst development and reactor technology; Catalyst research draws on complementary scientific skills: mineral synthesis, solid engineering, physical and chemical characterization of solids and, more recently, the use of theoretical approaches often based on density functional theory calculations. The choice of reactor technology is based on kinetic and thermodynamic considerations and also includes an initial assessment of the stability of the catalytic system.

Chemical and hydrodynamic reactor engineering; The main data to be acquired are kinetic measurements, mass and heat transfer, thermodynamic data, the impact of impurities on deactivation of the catalyst(s) and regeneration conditions.

Process schemes, simulation, heat integration and process optimization: This last phase of development is based on the set of data acquired in the development phase. It concerns the development of the complete process scheme with its list of equipment required to perform optimization and heat integration and to quantify the investment and operating cost for the given production capacity of the industrial unit. Process investment and operating costs are then determined;

These phases for process development will be illustred with specific situations regarding to biomass catalytic conversion towards fuel and chemicals.



Source: [2]

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INDUSTRIAL-SCALE PYROLYSIS FOR ENERGY AND PRODUCTS: WHICH OPPORTUNITIES TO PRIORITIZE?

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Sustainable Alternative Renewable fuels are key for decarbonisation of the transport sector: EU R&D programmes reflected this policy goal through supporting a variety of process pathway to liquid and gaseous biofuels, with a special focus on aviation, maritime and heavy duty. In this context, a renewed interest has grown around liquefaction processes, as fast pyrolysis or hydrothermal liquefaction: moreover, integration in biorefinery schemes combining biochemical and thermochemical processing has also attracted the attention of the industry and the technology developers.

The present work addresses the issue of industrial-scale biomass liquefaction through dry-wet thermochemical conversion. Following a short recall on the historical development of biomass fast pyrolysis, techno-economic assessments from literature of thermal and catalytic fast pyrolysis are discussed versus most promising short and medium/long market applications, identifying the development status of the major process steps. The potential for Pyrolysis Oil production in the EU is given. Reference to selected Fast Pyrolysis industrial projects in the EU is given, as well as major initiatives in the US.

Lignocellulosic, algal, and lipidic feedstocks, as well as lignin-rich streams are considered, placing these processes in the wider context of conventional and advanced biofuel technologies. Production costs are compared amont the various process routes, according to industry estimations.

The transport and CHP sectors as end-markets for Fast Pyrolysis Bio-Oil (FPBO) are presented, with the aim of discussing the most attractive opportunities for the medium term and thus trying to identify priority areas and opportunities. In fact, it seems is a very appropriate moment to consider the opportunity to focus (again) also on CHP use, and not necessarily on transports only: this approach would generate a significant impact on the fuel production and upgrading stage, compared to the work necessary for the production of a transport biofuel. This was a priority of several research works around FPBO in the ‘90s, that did not further developed also due to the framework conditions of the time.

As these considerations are fully policy-driven, reference to the EC proposal for Renewable Energy Directive (REDII) will be given, and key messages from the EU advanced biofuel industry (both production and use of Alternative Renewable Transport Fuels) given, with particular attention to pyrolysis oil. The main critical elements that could represents that can barriers for the deployment of the fast pyrolysis oil in the future will be remarked.

The work will also describe the existing experimental/pilot facilities and the projects being carried out at the University of Florence and RE-CORD in the field of Advanced Biofuels, with particular regards to the Aviation sector, such as the EU-Brasil H2020 BECOOL and the EU FP7 BIOREFLY projects, and their links to the topic under discussion.

Acknowledgments

The author wish to thank the European Commission, DG Research and DG Energy, support through the H2020 BECOOL project “Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels” and the EU FP7 BIOREFLY “Industrial scale demonstration biorefinery on lignin-based aviation fuels” project.

KEYNOTE LECTURES

HETEROGENEOUS CATALYSIS BY BASES FOR TRANSFORMATION OF RENEWABLES

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While heterogeneous acid catalysts is widespread, base-catalyzed reactions have been studied to a much lesser extent. An exploding interest in the last decade to heterogeneous catalysis by bases is strongly related to development of (lignocellulose) biorefinery concepts.

One of the key-reactions for valorization of lignocellulosic biomass is interconversion of aldose to ketose. Chemical conversion of glucose to fructose can be also done under alkaline conditions and at temperature higher than typically used (55-60 °C) for the enzymatic process. Transformations in alkaline environment following so-called Lobry de Bruyn-Alberda-van Ekenstein rearrangement are nonspecific leading to formation of side products. Aldose-ketose rearrangement is accompanied by epimerization which occurs in parallel to the main reaction. Other reactions, such as aldolization/retro-aldolization, β-elimination and benzylic rearrangement also contribute to formation of side products. Heterogeneous base catalysts would be of high interest being devoid of the apparent drawbacks of their homogeneous counterparts, such as low selectivity, and challenges with separation. In the lecture, our recent work on isomerization of glucose, galactose and arabinose to corresponding keto-sugars over a range of heterogeneous catalysts will be discussed [1]. Magnesium aluminates with different ratio between oxides resulting in materials with Mg/Al ratio from 0.2 to 0.9 were prepared, characterized and evaluated in terms of their catalytic behavior. The catalyst with Mg/Al ratio close to hydrotalcites was the most efficient considering activity, selectivity and stability. The sugar structure was shown to have a minor influence on catalytic activity and selectivity

Another potential way of transforming biomass is related to multistep conversion of cellulose to pentanol and hexanol. Further upgrading of these alcohols can be done by the Guerbet reaction, leading to 2-alkyl alcohols having a unique branching pattern. The reaction is complex comprising three different steps (Figure 1) requiring careful optimization to avoid side reactions. Generation of water can cause catalyst deactivation or side reactions. Recent efforts on the Guerbet reaction of C5-C6 alcohols using heterogeneous catalysts will be discussed.

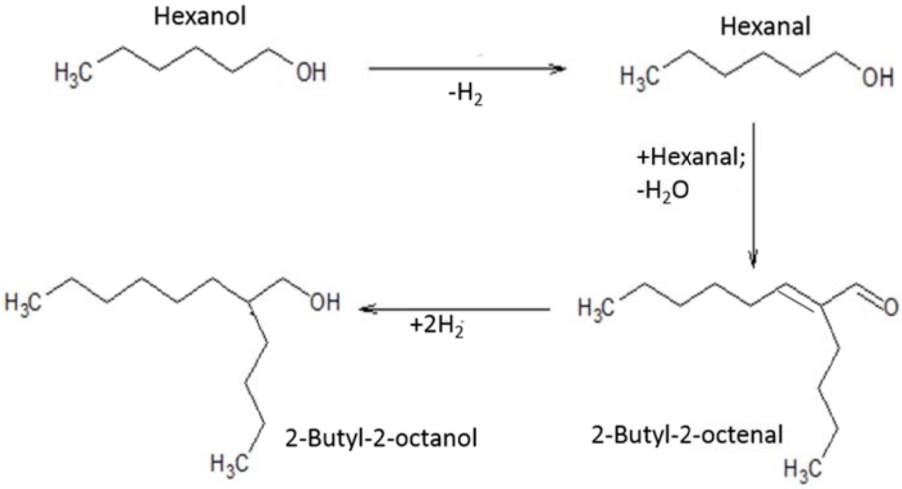

Figure 1. Guerbet reaction of 1-hexanol

The final example will be related to preparation of higher molecular weight compounds from short bio-derived carboxylic acids through decarboxylative coupling of acids (Figure 2) with formation of ketones. Ketonization of valeric acid on different metal oxides will be considered in detail [2].

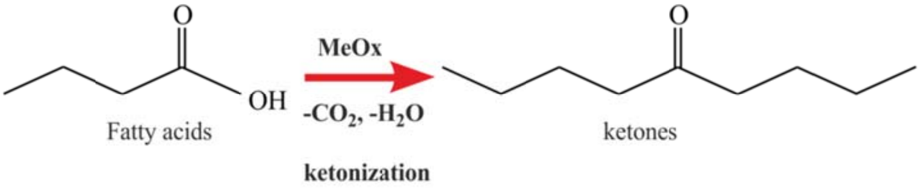

Figure 2. Coupling of a carboxylic acid on metal oxides

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KL-2

DESIGNER CATALYSTS FOR BIOFUELS SYNTHESIS

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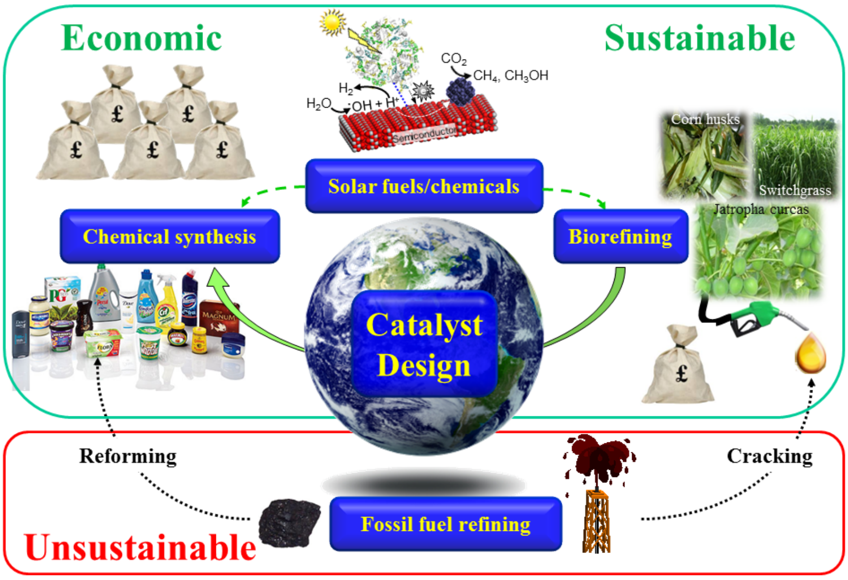
Concerns over dwindling oil reserves, carbon dioxide emissions from fossil fuel sources and associated climate change is driving the urgent need for clean, renewable energy supplies. If average global temperature rises induced by greenhouse gases are not to exceed 2 °C, then estimates indicate that a large proportion of oil, gas and coal reserves must remain untouched [1]. Biomass, derived from agricultural and forestry residues, or non-food sources of triglycerides are a sustainable source of carbon that can provide low cost solutions for transportation fuels and organic chemicals. Waste can become a key resource or feedstock, with the implementation of technology for biomass production and conversion predicted to generate ~15 Billion Euro income to the rural economy across the EU, with 16 % of transport fuel potentially supplied by waste derived biofuels by 2030, resulting in over 60 % reduction of GHG emissions [2]. Akin to petroleum refining, biorefining will integrate biomass conversion processes to produce fuels, power, and chemicals, thereby increasing the economic viability of bio-derived processes (**Scheme 1**). Indeed, the US DoE identified a range of sugar derived ‘Platform Chemicals’ produced via chemical or biochemical transformation of lignocellulosic biomass that would be potential targets for production in biorefineries [3].



Scheme 1. Biorefining versus Petroleum refining

KL-2

Catalytic technologies played a critical role in the economic development of both the petrochemical industry and modern society, underpinning 90 % of chemical manufacturing processes and contributing to over 20 % of all industrial products. In a post-petroleum era, catalysis will underpin bio-refinery technology, and researchers will need to rise to the challenge of synthesising chemical intermediates and advanced functional materials and fuels from non-petroleum based feedstocks [4].

This presentation will discuss the challenges faced in catalytic biomass processing, and highlight recent successes in catalyst design which have been facilitated by advances in nanotechnology and careful tuning of catalyst formulation. Specific case studies will explore (i) how the effects of pore architecture and acid strength can impact upon process efficiency in biodiesel synthesis [5], (ii) how catalytic pre-treatments improve transportation fuel production from pyrolysis oil, [6] and (iii) the role of bifunctional catalysts in the aqueous phase processing of sugars to important platform chemicals and fuel precursors such as 5-HMF derivatives [7,8]. Bilayer SO_4-ZrO_2/SBA-15 catalysts are one such example that will be discussed, which are hydrothermally stable mesoporous materials offering high acid site loadings and enhanced 5-HMF productivity from glucose over non-porous SO_4-ZrO_2 counterparts [9]. The co-existence of accessible solid basic/Lewis acid and Brönsted acid sites in grafted SO_4-ZrO_2/SBA-15 respectively promote glucose isomerization to fructose and dehydration of reactively-formed fructose to 5-HMF.

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PECULIARITIES OF POISONING DEGRADATION AND PLASMA-CATALYTIC LIGNIN REFORMING UNDER MICROWAVE IRRADIATION

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1. Introduction

One of the main problem for sustainable development today are creation of effective approaches to utilization of anthropogenic contaminants and creation of energy carries production base on organic wastes. Petroleum spilling and pollutants are one of the most important ecological problems of considerable current interest. Lignin is one of the renewable feedstock accumulated in large quantity every year as waster of wood treatment and paper cellulose industries. The stability of lignin polymer molecules is barrier to effective it treatment to useful products.

This abstract describes results of studies on the high-rate degradation of petroleum residues and pollutants adsorbed in the pores of carbon sorbents and plasma-catalytic lignin reforming to syngas under the action of microwave irradiation (MWI).

2. Experimental

Home-installation unit consist of an M-140 magnetron oscillation frequency, (2.45±0.05 GHz), was applied as a microwave radiation source; an ac power supply with a voltage of 220 V (50 Hz) was employed, and the voltage was regulated with a laboratory adjustable ratio autotransformer. The waveguide is connected to the MWI adsorption chamber (U-shaped vessel), in which due to the flow of water is realized the absorption of the residual irradiation. For microwave- assisted experiments quartz reactor was used (15 ml). Pore carbon sorbents possessed by high dielectric losses were selected for experiments. Ni and Fe-contained components were deposited on lignin surface. Conversion of phosphorous model compounds and tar adsorbed inner pores of carbon sorbents and lignin carried out in flux of Ar and CO_2 at temperatures 150-300 °C and 700-750 °C, stimulated by MWI, respectively. The tungsten–rhenium thermocouple, which was placed in a metal casing for microwave radiation shielding was used for temperature controlling in reaction volume.

3. Results and Discussion

Action of MWI on carbon sorbent led to plasma generation. Conversion of phosphorous model compounds and tar adsorbed inner pores of carbon sorbents with microwave stimulation rearched up to ~ 99 % for 10 min. H_2 was the main product in producing gas in case of microwave irradiation while the methane mainly formed by using convective heating.

In order to confirm the possibility of heavy oil residues processing into light hydrocarbons and hydrogen, a series of experiments by the decomposition of different classes of the individual hydrocarbons was carried out. It was found that in case of MWI cracking of C-H bond dominated. This fact explains an increased hydrogen yield in comparison with convection heating where cracking C-C bond dominates[1].

Dry reforming (DR) of lignin with supported different content of Ni and Fe nanoparticles under microwave irradiation (MWI) with plasma generation has been studied[2]. After 10 min of DR at 700-750 °C recovery of H_2 from lignin reach up to 80 % and the H_2/CO ratio of ~1/1 at summary conversion of the lignin organic mass- 65 %. The maximum selectivity relates to syngas forming in DR process was achieved up to 90% when combination of Ni-Fe active components has been forming on lignin surface.

The structure of Ni and Fe -containing lignin samples before and after reforming were investigated by XRD, TEM, EDA, Mossbauer spectroscopy and magnetic measurements. It was studied “operando” conversion of organic part contained in lignin by vibration spectroscopy.

4. Conclusions

The test method of the high-rate destruction of tar and other phosphorous contained pollutants under the action of microwave irradiation differs from traditional thermal decomposition methods. It makes it possible to utilize refinery waste in short time with the production of valuable components.

MWI noticeably intensifying dry reforming of lignin contained Ni and Fe as well as Ni-Fe contained nanosize particles into syngas. For 10 min practically 80-90 % H_2 eliminated from initial lignin.

Enhanced contribution of metal components in the conversion of lignin to syngas comparison with its conversion without active components and results obtained at convective heating allows to classifying process as the plasma-catalytic.

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Acknowledgements

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DME SYNTHESIS BY CO_2 HYDROGENATION ON HYBRID CATALYTIC SYSTEMS

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The production of dimethyl ether (DME) by hydrogenation of CO_2 is an issue that recently is receiving particular attention [1-2]. As well known, in order to obtain DME *via* this direct reaction it is necessary that catalyst possesses a multi-functionality, as the reaction proceeds through the consecutive steps of methanol formation and subsequent dehydration to DME [3-5]. In general, first methanol is generated by interaction of activated hydrogen and CO_2 on metal-oxide sites, while DME is then formed by dehydration of methanol (MeOH) on acid sites [3,5,6]. Generally, a mechanical mixture of mixed oxides (containing Cu as active species for the synthesis of methanol) and a zeolite, typically ZSM-5 [7-8], has been mainly proposed as an effective catalytic system. In particular, some fundamental aspects have been indicated as crucial for high process productivity: i) the zeolite must be stable in presence of water; ii) the formation of olefins should be inhibited; iii) the acid sites must be well distributed and of suitable strength.

Here, the one-step CO_2 hydrogenation reaction to dimethyl ether (DME) on novel hybrid Cu-ZnO-ZrO_2–Zeolite catalytic system will be investigated with the aim to better define the way to achieve high DME productivity. Catalytic results, in terms of CO_2 conversion and product distribution using a fixed bed reactor will be discussed to individuate the optimal reaction conditions to ensure both high CO_2 conversion per pass and high CH_3OH/DME selectivity. Particular attention will be addressed to compare the different opinions on reaction mechanism proposed, so to ascertain what is the controlling step preventing the achievement of high CO_2 conversion at temperature lower than 473 K. An effort will be also profuse to precisely individualize, in the hybrid systems, the active sites for H_2 and CO_2 activation by correlating the results as a function of their nature and strength. Furthermore, the influence of structure and morphology of catalyst on mass transferring reaction intermediates will be considered to highlight how these parameters can affect DME/MeOH production.

On the whole, it has been found that the efficiency in DME production of hybrids systems strongly depends upon several factors. The typology of zeolite employed, the distribution of surface oxides, the strength of acid sites are the main factors that play a fundamental role in driving the reaction towards CH_3OH, DME or CO formation [9]. In particular, the pore structure of zeolite was found to be more suitable for the generation of a larger population of Lewis basic sites necessary in CO_2 activation step, also favoring easier accessibility to the Brønsted acid sites essential for the MeOH-to-DME dehydration step [10]. The comparison of the process productivity of multifunctional systems at 260 °C and 5.0 MPa disclosed the superior behavior of hybrids system with respect to classical mechanical mixtures, leading on the CuZnZr-FER hybrid system a final DME_{STY} higher than 600 $g_{DME}/Kg_{cat}/h$.

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KL-5

RESEARCH AND EVALUATION OF BIOMASS PYROLYSIS

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For decades, fast pyrolysis has been advocated to be a promising technology for the production of a bio-oil which can be further upgraded or refined for electricity, transportation fuels and chemicals production. At the time of writing, several demonstration factories are considered worldwide aiming at maturing the technology. Yet, slow market introduction of the technology and adverse properties of the bio-oil point out room for improvement.

In this paper, firstly, an historical account will be given on the research into fast pyrolysis of biomass. Research focusing on understanding the underlying processes at all relevant scales, ranging from the chemistry of cell wall deconstruction to optimization of pyrolysis factories, in order to produce better quality oils for targeted uses will be discussed. Most attention will be given to i) the interplay of chemistry and transfer processes at cell wall level (see figure 1 for an example), and ii) the use of catalytic activity to steer the product quality (see figure 2). This first part will be illustrated by results from the open literature and data obtained in our own laboratory in the last 30 years.

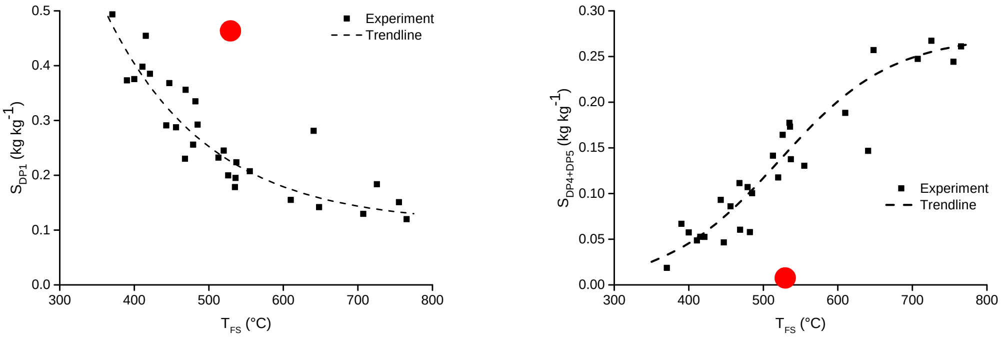

Figure 1. Results of cellulose pyrolysis; yields versus temperature. Left: yield of levoglucosan (DP_1). Right of DP_4 + DP_5 (large ologomers). Black symbols: results at 5 mabr, red symbol: 1 bar. *These results indicate that the production of levoglucosan is induced by lower evaporation rates (mass transfer limitation) at 1 bar compared to 5 mbar which results in pronounced times of oligomers to react on the particle. Evidence is accumulating that both the distribution of the polymerization degree of the produced sugars and the mass loss rate of cellulose is determined by the interplay of chemistry, heat and unequivocally mass transfer at cell wall level. React. Chem. Eng., 2016,* ***1****, 555-566.*

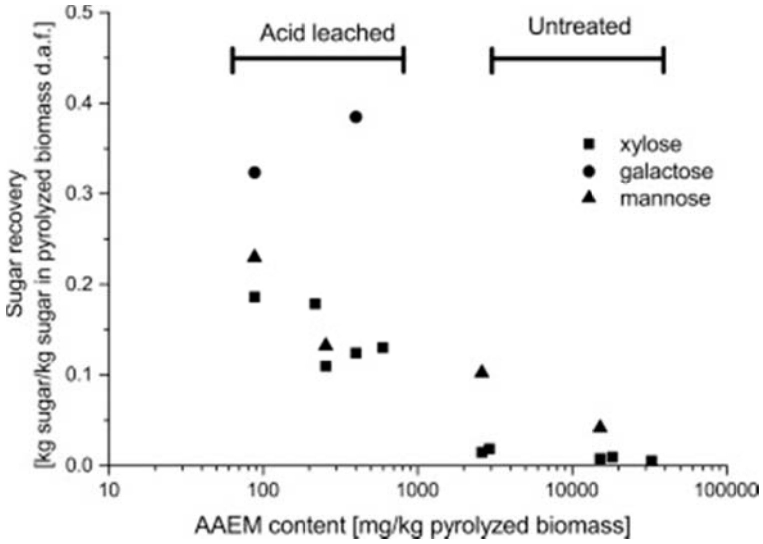

Figure 2. Sugar yield from the pyrolysis of pine wood, straw, hay and bagasse as a function of the alkaline and alkaline earth metals (AAEM) in the biomass.
Lower AAEM levels were obtained by acid leaching.
These results clearly show the (huge) catalytic activity of the AAEMs present in biomass.
Journal of Analytical and applied Pyrolysis, 2015, 116, 253-262.

Secondly, the author will present an evaluation of pyrolysis processes indicating how the in the years to come the scientific community could advance in obtaining better control of the processes happening in these processes and consequently of the oils produced. The potential of biomass pyrolysis for the production of transportation fuels, sugars, phenols, light oxygenates and thermoplastic materials will be assessed.

DEVELOPMENT OF NEW INTEGRATED CATALYTIC PROCESSES OF LIGNICELLULOSIC BIOMASS VALORIZATION INTO VALUABLE CHEMICAL PRODUCTS

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The renewable resources of wood are large in the Russia and in many other countries. But at present the low-grade wood and waste wood are little used to produce bulk and fine chemicals. This presentation describes the new approaches to catalytic biorefinery of different types of wood based on integration of optimized processes of valorization of main components of wood biomass with the use of green reagents and solid catalysts.

Air dry sawdust (fraction 2-5 mm) of aspen-wood, birch-wood, abies-wood, pine-wood and larch-wood were used as initial raw materials. Catalytic processes of wood thermal conversions were studied with the use of stirring fixed-bed reactors. FTIR, XRD, SEM, solid state ^{13}C CP/MAS and chemical methods were used for study the solid products. Low molecular mass products were identified by GC, HPLC and GC-MC methods.

The developed processes use as a key stage the catalytic fractionation of wood on polysaccharides and lignin. Three different ways of wood catalytic fractionation were researched, namely, peroxide oxidation in the mixture of acetic acid – water, aerobic oxidation in alkaline medium, thermal conversion in supercritical alcohols (see Figure).

Solid catalysts TiO_2, CuO, high-silica zeolites, $NiCu/SiO_2$, $NiCuMo/SiO_2$ and optimal process conditions were selected for conversion of wood biomass to cellulose, aromatic aldehydes and liquid hydrocarbons.

This presentation provides examples demonstrating the feasibility of obtaining valuable chemicals and cellulose with rather high yield by catalytic biorefinery of hardwood and softwood with the use of solid catalyst and green reagents.

Catalytic oxidation of hardwood and softwood by H_2O_2 in acetic acid – water medium under optimized mild conditions ($\leq$ 100 °C, 1 MPa) over TiO_2 catalyst makes possible to achieve the effective separation of wood biomass components on microcrystalline cellulose and soluble products from lignin and hemicelluloses.

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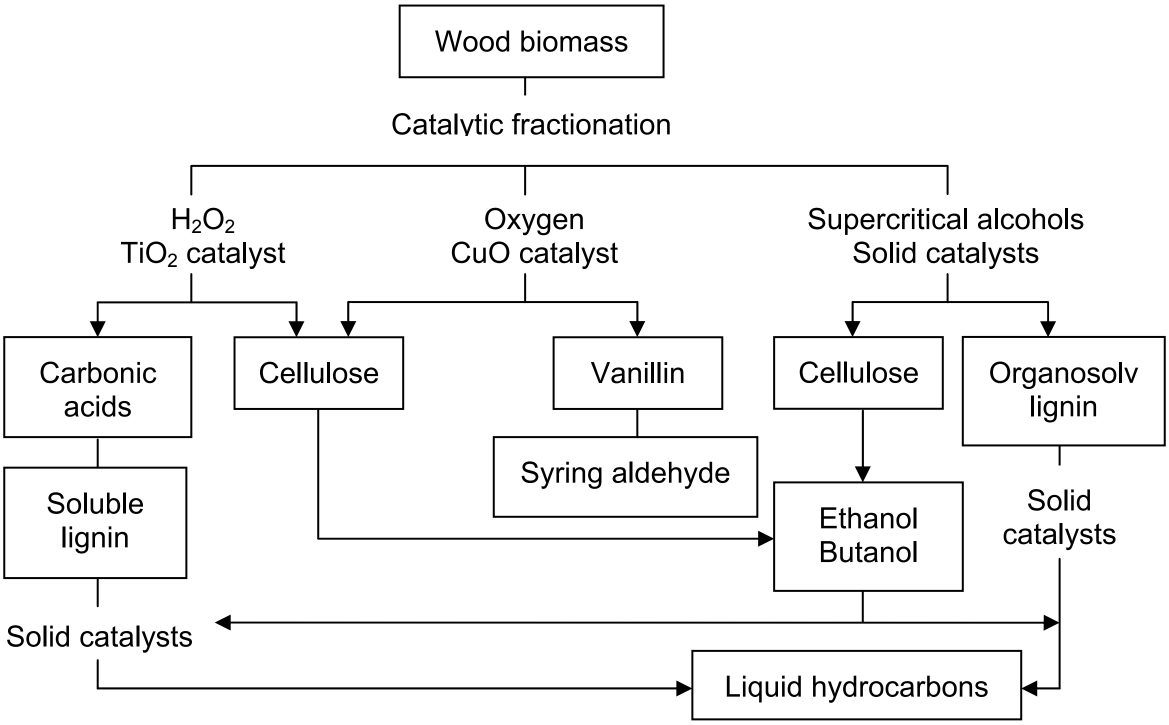

Figure. Scheme of wood biomass biorefinery based on the use of green reagents and solid catalysts

Oxidation of wood biomass by O_2 in alkaline medium over CuO catalyst allows to separate at 160-170 °C softwood on cellulose and vanillin and hardwood – on cellulose and the mixture of vanillin and syring aldehyde.

Thermal conversion of mechanically activated aspen-wood in supercritical ethanol at 270 °C in the presence of high-silica zeolite catalysts increases by 2.5 times the yield of liquid hydrocarbons as compared to non-catalytic process.

The optimal conditions and effective catalyst $NiCuMo/SiO_2$ were selected for the process of organosolv lignins depolymerization in supercritical butanol and ethanol which insure the high yield of liquid hydrocarbons at 300 °C (to 89 % mas.).

Acknowledgements

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ORAL PRESENTATIONS

Section I. CATALYSIS IN DENDROCHEMISTRY FOR VALUABLES PRODUCTION

Catalytic systems for hemicellulose depolymerization
Catalytic processing of tall oil and tar, Selective conversion of sugars
Catalytic transformations of CO_2 to fine chemicals

DIRECT CATALYTIC CONVERSION OF CELLULOSE TO LIGHT HYDROCARBONS OVER Pt/NH_4-USY ZEOLITE CATALYST AT LOW TEMPERATURE

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Introduction

Renewable resources are attracting increasing attention as substitutes for fossil resources. Among them, biomass cellulose offers numerous advantages as a ubiquitous feedstock. Recently, we have reported an one-pot direct conversion of cellulose to C_3 and C_4 hydrocarbons over Pt/H-zeolite catalysts at 443 K under hydrothermal conditions without hydrogen [1-3]. Results revealed that the activity and selectivity were affected by the zeolite structure and the supported state of Pt. However, the hydrocarbon yield remained still low. Therefore, development of highly active catalyst and optimization of reaction conditions were conducted. Effect exerted on the activity and selectivity by the catalyst preparation method and the reaction time were investigated. The relation between the supported state of Pt and the results for catalytic activities was also elucidated.

Experimental

Pt/NH_4-USY zeolite catalyst was prepared using an ion-exchange method according to a published procedure [4] with some modifications; 1 wt % Pt was supported on NH_4-USY(14) zeolite, with the number in parenthesis representing the SiO_2/Al_2O_3 ratio. Hexachloroplatinic(IV) acid was used as the precursor of supported Pt. The obtained powder was calcined at 803 K for 30 min in 6 % H_2/N_2 gas flow (100 mL min^{-1}).

Catalytic reaction was performed in a batchwise autoclave (30 mL, SUS 316). Cellulose powder (microcrystalline, MP Biomedicals Inc.) was pre-treated using a planetary ball mill to produce fine particles. Reaction conditions are follows; catalyst: 0.25 g, cellulose: 0.25 g (8330 C-μmol), water: 20 mL, temperature: 443 K, reaction time: 3–72 h, Ar atmosphere. The reaction products were analyzed by GC-FID, GC-TCD, TOC, and HPLC.

Results and discussion

Catalytic activity of the prepared Pt/NH_4-USY(14) catalyst was compared to that of a previously reported Pt/H-USY(14) [2]. Figure 1 presents results of activity tests over Pt/NH_4-USY and Pt/H-USY catalysts at 443 K for 3–72 h of the reaction time. For all reaction time courses, Pt/NH_4-USY catalyst showed higher cellulose conversion and higher C_3+C_4 hydrocarbon yield than reactions over Pt/H-USY catalyst. To improve the C_3+C_4 hydrocarbon yield, the effect of reaction time on the activity was also investigated. Over the Pt/H-USY catalyst, the C_3+C_4 hydrocarbon yield increased with increased reaction time up to 18 h, then it reached a plateau. However, over the Pt/NH_4-USY catalyst, the C_3+C_4 hydrocarbon yield increased concomitantly with the increased reaction time; the C_3+C_4 hydrocarbon yield reached 16.0 C-% at 72 h.

To clarify differences of catalytic activities, the Pt particle size was evaluated using a CO chemisorption. The Pt particle sizes were 5.4 nm for Pt/NH_4-USY(14) and 8.9 nm for Pt/H-USY(14). Further investigation for the effect of Pt particle size on the catalytic property will be conducted.

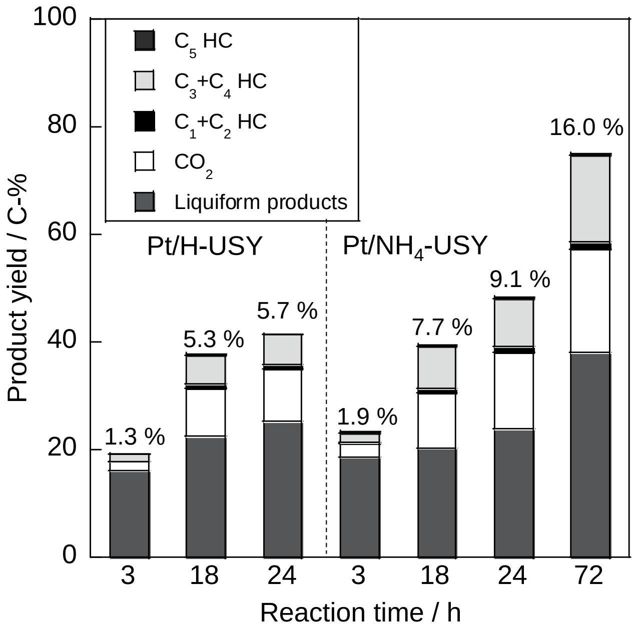

Fig. 1. Time course of product yield in the cellulose conversion over Pt/H-USY(14) and Pt/NH_4-USY(14) catalysts at 443 K. Values in the graph denote C_3+C_4 hydrocarbon yield

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CELLULOSE BIOREFINERY BASED ON COMBINED CATALYTIC AND BIOTECHNOLOGICAL APPROACH FOR PRODUCTION OF 5-HMF AND ETHANOL

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The instability on the global energy and hydrocarbon feedstock markets as well as necessity to diminish the emission of CO_2 leads to an increasing trend toward the development of sustainable technologies that employs locally available sources of the renewable feedstocks for the production of fuels and valuable chemicals [1-3]. For this purpose the modern biorefineries are developing for the conversion of lignocellulosic biomass into a spectrum of marketable products and energy. The lignocellulosic biomass itself consists of complex biopolymers comprising cellulose (40-60 %), hemicelluloses (20-30 %), and lignin (10-30 %) [4]. Sugar monomers can be derived from biomass by hydrolysis with soluble catalysts like mineral acids, alkalis and enzymes. However, the main disadvantage of such type of catalysts is a need for separation from the products and their regeneration after the reaction. To avoid this problem the carbon-based solid acid catalysts may be used for the hydrolysis of cellulose and its conversion into the valuable products via the one-pot process. The combination of cellulose hydrolysis into glucose and its subsequent dehydration into 5-hydroxymethylfurfural (5-HMF) [5-7] will produce the platform molecules as a feedstock for manufacturing of a wide range of products (diesel and jet fuels, plastics, etc.).

The aim of this study is to examine the combination of the one-pot catalytic process of cellulose conversion into 5-HMF and glucose over a solid acid catalyst and a biotechnological process of the glucose fermentation with thermotolerant yeasts into ethanol.

Mechanical activation of microcrystalline cellulose was performed in a planetary mill «Pulverizette 5» during 40 min with the acceleration of 22 g. The size of the cellulose particles was measured by optical microscopy with a digital camera. The degree of crystallinity of cellulose was calculated using XRD study data as the ratio of the peak area of crystalline cellulose to the total area of all peaks.

The one-pot hydrolytic dehydration of the mechanically activated microcrystalline cellulose into glucose and simultaneously 5-HMF was conducted in water in the presence of a solid acid catalyst. As such catalyst we used a mesoporous graphite-like carbon material Sibunit-4, which was oxidized in an environmentally friendly manner by wet air [7-8]. The process was performed at a temperature of 180 °C and a pressure of 1 MPa of argon under the vigorous mechanical stirring (1500 rpm). The activated cellulose (10 g L^{-1}) and the catalyst (10 g L^{-1}) in water (45 mL) were incubated for 5 h. During the reaction the composition of the reaction mixture were analyzed by HPLC. The recorded yields of glucose and 5-HMF were 21.1 – 25.1 and 6.6-9.4 %, respectively, while the fructose, mannose and organic acids were found in minor concentrations.

Also we revealed that extraction of catalytic hydrolyzate of cellulose with organic solvents (n-butanol, isobutanol and MIBK) can effectively recover the 5-HMF from aqueous solutions of sugars. Diethyl ether was found to be poor extractant. Isobutanol was selected for the 5-HMF extraction in this study due to its effectiveness. 5-HMF was separated from the solvent by distillation. The structure and purity of the isolated 5-HMF was confirmed by ^{1}H and ^{13}C NMR.

A relatively low content of fermentation inhibitors (including 5-HMF) and compete absence of furfural in the mixture obtained after the extraction of 5-HMF allowed the production of ethanol via fermentation with a relatively high efficiency. It should be noted that in this case, ethanol is a byproduct of the 5-HMF production, which allows the complete recycling of catalytic hydrolysates of cellulose. Application of thermotolerant yeasts for the fermentation at 42 °C will also reduce production costs. Compared with other methods of producing ethanol from hydrolysates (for example, the acid hydrolysis treatment and AFEX) the catalytic process is recognized as an environmentally safely process. It is shown that the use of strains *K. marxianus* C1 and *O. polymorpha* CBS4732 for the fermentation of processed catalytic cellulose hydrolysate has a relatively high efficiency since the strains are resistant to fermentation inhibitors. Thus proposed combination of a catalytic processing of mechanically activated cellulose for the 5-HMF production and subsequent fermentation of extracted hydrolysate with thermotolerant yeasts may be a promising alternative method for the ethanol production by fermentation and can be used to produce other valuable substances.

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ENVIRONMENTALLY BENIGN CATALYTIC OXIDATION FOR FINE CHEMICALS SYNTHESIS

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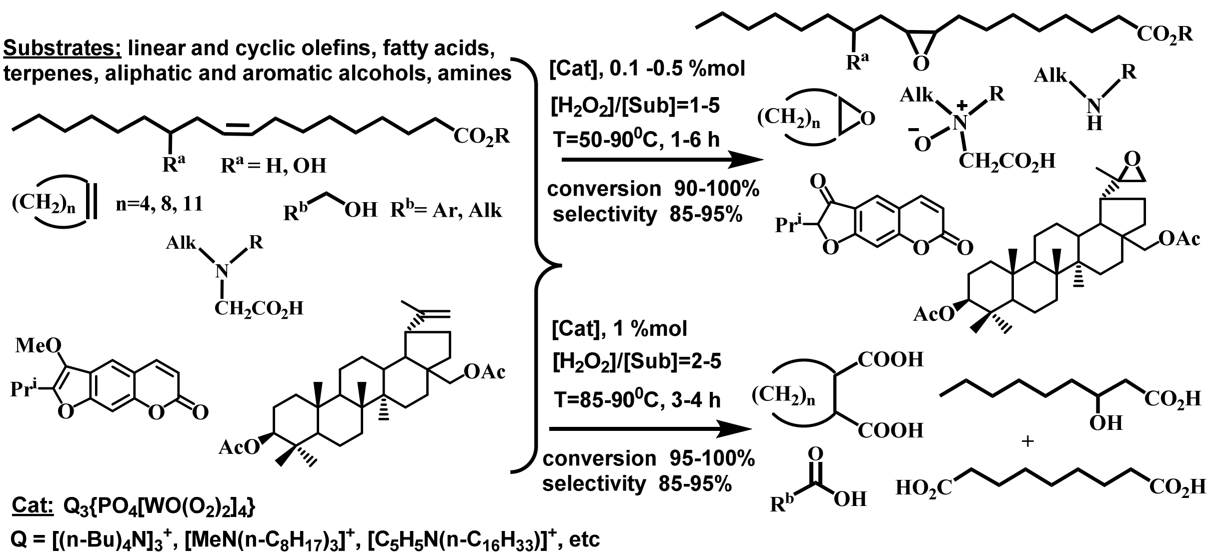
Oxidation of organic substrates with hydrogen peroxide in the presence of peroxopolyoxometalates in combination with phase-transfer catalysts is an efficient green route for producing fine chemicals having various functional groups. The process takes place in mild conditions with good conversion and selectivity, without the use of organic solvents and explosive oxidants. Two-phase reaction media (organic phase - water phase) facilitates the separation of catalyst and products remaining in different phases. This methodology has considerable potential for the development of green catalytic processes of selective oxidative modification of available organic feedstock to produce valuable chemicals.

The structure of the catalysts composed of peroxopolyoxometalates and quaternary ammonium cations was studied using EXAFS, IR, and Raman spectroscopy in order to determine the influence of the structure on the catalytic properties. Catalytic oxidation of aromatic and aliphatic alcohols, linear and cyclic olefins, terpenes, unsaturated fatty acids (UFA), amines and amino acids resulted in formation of epoxides, carbonic acids, and N-oxides with high conversions (90-100 %) and selectivities (85-95 %). Processes were carried out using hydrogen peroxide water solutions (25-35 %) as oxidant, at atmospheric pressure, temperatures not higher than 90 °C, and low catalysts concentrations (0.1-1 mol. % against substrate).

Oxidation of UFA from non-edible oils in the presence of these catalysts is the efficient green method for selective producing of aliphatic epoxides, mono- and dicarbonic acids with yields up to 90 %. The best results were obtained with the use of methyl-tri-*n*-octyl ammonium tetra(diperoxotungsto)phosphate as a catalyst. Epoxidation of oleic acid (the main constituent of tall oils) and ricinoleic acid (the main constituent of castor oil) successively proceeds in solvent-free conditions with the catalyst concentration of 0.07-0.1 mol. %. Formation of mono- and dicarbonic acids occurs with high selectivity (83-85 %) and nearly 100 % substrate conversion at catalyst concentration of 1 mol %.

OP-I-3



Scheme 1. Oxidation of various substrates using ammonium peroxopolyoxotungstates as catalysts

The catalysts were applied to the mild-conditions oxidation of natural products of complex structure. Betulin is a triterpene isolated from birch bark. It possesses a wide spectrum of valuable biological activities and is regarded as a precursor for synthesis of antivirus and anticancer pharmaceuticals. The highest selectivity of the reaction of betulin diacetate oxidation was achieved at 60 °C in 4 h.

Peucedanine is a plant furanocoumarin isolated from the roots of hog's fennel, which is used in traditional medicine in treatment for cancer. Oxidation of peucedanin easily proceeds at 60 °C in 1 h with low catalyst loading and more than 5-fold oxidant excess selectively yielding 2-hydroxyoreoselon.

This method was employed for N-phosphonomethyl iminodiacetic acid oxidation with obtaining its N-oxide in 96 % yield at 70 °C. Oxidation of the same substrate at 85 °C in the presence of 0.1 mol % methyl-tri-*n*-octyl ammonium tetra(diperoxotungsto)phosphate afforded N-phosphonomethyl glycine (glyphosate, worldwide used non-toxic herbicide) in up to 92 % yield.

Therefore, the green catalytic routes for valuable products synthesis starting both from renewable plant feedstock and from petrochemicals have been developed. The products have been obtained with high conversions (90-100 %) and selectivities (85-95 %) using water solutions of hydrogen peroxide and low catalyst loading.

Acknowledgements

This work was supported by Russian Foundation for Basic Research, Project 16-29-10691.

ORAL PRESENTATIONS

Section II. BIOMASS DERIVATIVES IN PETROCHEMISTRY

Catalyst application for clean syn-gas and clean hydrogen production
Lipids in petrochemical synthesis
Co-processing of biomass derivatives and oil feedstock

ROLE OF ALUMINUM IN Ni-Co STRUCTURED CATALYST FOR DRY AND STEAM REFORMING OF METHANE; HYBRID REACTOR FOR SYNGAS AND HYDROGEN CO-PRODUCTION

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Porous ceramic membrane-catalytic converters produced by self-propagating high-temperature synthesis (SHS) from Ni(Al)-Co_3O_4 powders were used for dry and steam reforming of methane. Precursors included a Ni metal powder containing 0-15 mass % of aluminum and a cobalt oxide (II, III) powder. The converter is a hollow tube with one sealed end. Feedstock supplied on the outer surface of the converter wall in order to arrange forced diffusion of the substrate in a spatially confined volume of pores containing catalytically active components.

It was shown that chemical transformations in the channels of a porous ceramic catalytic converter proceed much more intensively than in a conventional fixed-bed reactor. According to kinetic studies, the intensification of the process in the catalytic channels of the converter is a consequence of improved mass and heat transfer. Previously it was found that converter with mass ratio Ni/Co_3O_4~1 showed the most pronounced synergistic effect in comparison with other mono- and bimetallic catalysts. In dry reforming of methane granulated catalyst prepared from converter's material showed 2.2 times lower productivity than structured catalyst of the same composition (85 000 vs 39 000 $l/(h \cdot dm^3_{cat.})$). It is important to note that results obtained using monometallic converters consisting only of nickel or cobalt were approximately 3-5 times lower.

Phase composition evolution of the catalytic converter was studied by SEM, TEM, XRD. It was shown that during SHS aluminum additive led to reduction of Co_3O_4 and formation of α and γ-Al_2O_3, with Ni-Co alloy nanoparticles (10-50 nm) on its surface.

It was established that aluminum introduced by mechanoactivation leads to greater catalytic performance than aluminum introduced by mechanical admixture. Addition of 5 % aluminum allows to achieve the highest productivity in comparison with other studied concentrations of Al due to formation inactiv Ni_3Al.

The original hybrid reactor consisted of Ni(Al)-Co-containing converter with integrated Pd-Ru membrane was developed. The construction allowes to carry out simultaneous processes of highly efficient steam and dry reforming of organic substrate into syngas and in situ hydrogen separation. Removal of hydrogen decreases reaction temperature and increases overall efficiency of hydrogen production.

It was demonstrated that in dry reforming of methane selective removal of hydrogen from reaction zone using Pd-Ru membrane allowed to increase methane conversion from 42 % up to 72 % in comparison with traditional reactor “contactor”. Feeding the substrate at a rate of 9 L/h and T = 700 °C hydrogen productivity was 7.2 L/h and hydrogen recovery achieved 87 %. It was found that in steam reforming of methane using of the integrated reactor increased methane conversion. It was determined that increasing of pressure increased hydrogen recovery up to 65 % whereas methane conversion rate still constant.

Acknowledgements

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OP-II-2

THE INTERPLAY BETWEEN MASS/HEAT TRANSFER AND CHEMISTRY IN LIGNIN FAST PYROLYSIS

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This work aims at advancing the understanding of reactions and transport phenomena and their interplay by studying the relative effects of the reaction rate, the heating rate, the escape rate of volatile products from the pyrolyzing lignin particles and the rate of the subsequent quenching of these products. To this end, a screen-heater reactor has been designed that combines a high heating rate (5000 °C/sec.) of the lignin sample with fast removal (milliseconds) and quenching of reaction products, see Figure 1. Hence, the objective of the screen-heater is to minimize the effects of so-called secondary reactions in an attempt to study the first stages of the lignin pyrolysis process.

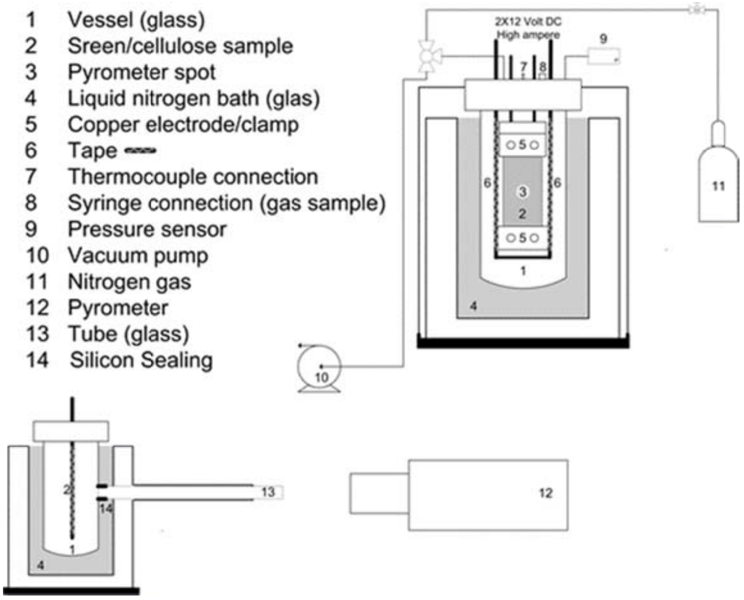

Figure 1. Schematic representation of the screen-heater set-up

The experiments were performed at a pressure of 5 mbar and 1000 mbar with temperatures varying between 300 and 700 °C. In this work kraft lignin, pyrolytic lignin and lignin model compounds, representing different bonds (e.g. C-C, C-O), were used as feedstock. The obtained oils were analyzed using GC/MS, GPC and NMR.

It was found that under vacuum around 80 wt % of the lignin could be recovered as oil with only very little amounts of gas produced (<1 wt %). The amount of oil significantly decreased at atmospheric pressure and more than twice as much char is produced compared to vacuum pyrolysis. Evaporation of a part of the original lignin feedstock was responsible for a significant part of the recovered oil but clearly cracking reactions did occur within milliseconds after which the cracked feedstock could be evaporated or physically entrained. The DCM soluble (light) fraction (~50 wt % of the lignin feedstock) could be evaporated to a large extend. In all cases, large aromatic oligomers seem to be the primary products of lignin pyrolysis.

COMPOSITIONAL DEPENDENCE OF VISCOSITY FOR CRUDE OILS

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Up to date crude oil remains to be the main sourse of energy. But inspite of the availability of sophisticated technologies and existing equipment there are still problems involved in oil production, processing and even transportation. The fundamental reason for the permanent development of the new technological solutions is the depletion of «easy» hydrocarbon resources, i.e. light crude oil. Thus, developing of technologies appropriate for heavy oils is especially important as they are to become the main raw material for petrochemical industry.

Rheology can be used to characterize oil properties and to solve some of the problems with heavy oil transportation. Then it is necessary to estimate the input of the main chemical oil components and its disperse structure into their viscosity.

Crude oil contains thousands of individual components, which are traditionally divided into 4 main groups: saturates, aromatics, resins and asphaltenes (so called SARA-analysis). The detailed study of these fractions influence on the oil viscosity can help to decrease it up to the suitable level.

Experimantal and referenced data of about 200 oil samples were used to find general correlations between their viscosities and compositions. It was found that oil viscosity increase with growing content of aromatics, resins and asphaltenes while the increase of the saturates content results in the decrease in viscosity. It is worth noting that similar correlations are of general value for oils of various origins.

According to the obtained results we have found that asphaltenes from all crude oil samples acted as promoters of the viscosity growth at rather low concentrations (less than 5 wt. %).

Meanwhile the concept of «asphaltene» is not univocal as it includes rather wide range of organic matters. It was shown that precipitation of different types of asphaltenes from heavy crude oil greatly effects its viscosity (it can be decreased by 2-3 orders). This result clearly shows that it can be treated as the method of decreasing viscosity of heavy crude oil to the necessery low level for its transportation.

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CONVERSION OF PYROLYSIS OIL TO SYNTHESIS GAS THROUGH AUTOTHERMAL REFORMING OPERATED IN A MINIPLANT IN AN MODULAR CONTAINERISED ENVIRONMENT

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BIO-GO-For-Production is a Large Scale Collaborative Research Project co-ordinated by the presenting author. It aims at the conversion of biogas and pyrolysis oil to synthetic gasoline by reforming, methanol synthesis and methanol-to-gasoline steps. The catalyst development work is supported by modelling, kinetic analyses and in-situ studies. The catalyst technology developed is validated by an extended miniplant operation of combined biogas and pyrolysis oil reforming, methanol synthesis and gasoline production via the MTG process to verify the feasibility of the concept.

The reforming of pyrolysis oil has been subject to numerous studies, however, the larger part of investigations to-date deals with the conversion of model compounds, surrogates of bio-oil or the aqueous phase of it. Only few publications have the conversion of crude pyrolysis oil through reforming as subject. In most cases substantial coke formation was observed [1-4] and high reaction temperatures in the range from 800-900 °C along with a substantial surplus of steam (S/C $\geq$7) to suppress coke formation are required [1, 5].

The presentation will focus on first results of miniplant operation with emphasis on the autothermal reforming of crude pyrolysis oil and the synthesis gas purification steps downstream.

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DEVELOPMENT OF THE BIFUNCTIONAL Ni-PHOSPHIDE CATALYSTS FOR METHYL PLAMITATE HYDRODEOXYGENATION

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The limited reserves of fossil fuel, economical and ecological problems stimulate the search and development of alternative sources of fuels. Biofuels attract much attention as sustainable and “green” fuels. Hydrodeoxygenation (HDO) of triglyceride-containing feedstocks such as nonedible vegetable oils, waste fats from the food industry, used cooking oil and animal fats is one of a promising technology to convert these crudes into diesel fuels – “green diesel” or “renewable diesel” [1]. Sulfided NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalysts are active in these reactions but it is essential to add sulfur-containing compounds to the feed in order to maintain the catalyst activity. Transition metal phosphides are a promising alternative, they are active, stable and do not contain sulfur. Ni-phosphide catalysts are the most active among phosphide catalysts in many reactions (hydrodesulfurization, hydrodenitrogenation and hydrodeoxygenation). The most popular method to prepare Ni-phosphide catalysts is the temperature-programmed reduction (TPR) of phosphates in hydrogen flow. After reduction PO_x residues remain on the support surface among with Ni-phosphide particles. These PO_x groups may have P-OH acid sites which can catalyze hydrolysis and dehydration reactions of HDO [2]. There is another technique to synthesize Ni-phosphide catalysts without PO_x residues – in situ phosphidation of metallic Ni by PPh_3.

The aim of the present work is to demonstrate bifunctional nature of SiO_2 and γ-Al_2O_3-supported Ni-phosphide catalysts, prepared by different techniques, with different amount of PO_x groups in HDO of a vegetable oil model compound – methyl palmitate ($C_{15}H_{31}COOCH_3$).

The catalyst precursors for TPR were prepared by impregnation of the support with aqueous solutions of $Ni(OAc)_2$ and $(NH_4)_2HPO_4$ or $Ni(OH)_2$ and H_3PO_3 (Ni/P=1/2) followed drying and reduction in hydrogen flow. The precursors for in situ phosphidation were prepared by impregnation of the support with aqueous solutions of $Ni(OH)_2$ and citric acid (Ni/CA=1/2). The catalysts were characterized by elemental analysis, N_2 physisorption, H_2-TPR, XRD, TEM. The catalytic experiments were carried out using fixed-bed continuous flow reactor at 290 °C and 3.0 MPa.

XRD analysis confirmed that Ni_2P phase (the most active phase for HDO) forms after in situ phosphidation (at 380 °C) in SiO_2 and γ-Al_2O_3-supported samples. TPR method (at 550-650 °C) did not allow us to synthesize Ni_2P phase over γ-Al_2O_3-supported samples due to strong interaction of phosphates with the support. Thus Ni_3P and $Ni_{12}P_5$ phases form over γ-Al_2O_3-supported samples. Due to small initial metal particles (<2.5 nm) after in situ phosphidation forms small particles of Ni_2P (<2.5 nm). Contrary, after TPR on the surface of the supports form larger particles (10-100 nm) with broad particle size distribution due to high temperatures used in this method. But in methyl palmitate HDO activity of TPR samples (even for γ-Al_2O_3-supported samples) is higher. This fact can be explained by the necessity of bifunctional nature of the catalyst for HDO of the aliphatic ester. We have previously shown that hydrolysis of the ester to the acid is the rate-limiting step [2]. The transformation of acid is significantly faster than the transformation of ester. Thus, increasing of the first reaction – hydrolysis of methyl palmitate allows one to increase overall HDO process.

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OP-II-6

LOW-TEMPERATURE CATALYTIC SYNGAS PRODUCTION FROM BIO-METHANE OVER La DOPED Ni/ZrO$_2$ CATALYST IN AN ELECTRIC FIELD

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Introduction

The process of dry (carbon dioxide) reforming of methane (DRM), as shown in following equation, is ideally a 'green' hydrogen production process from the viewpoint of an environment and energy aspects because both methane and carbon dioxide are greenhouse gases [1]. Biogas, composed of methane and carbon dioxide in almost equal concentrations, is useful as a raw material for the DRM reaction.

$$CH_4 + CO_2 \rightarrow 2CO + 2\ H_2\ \Delta H_0^{298} = 247.2\ \mathrm{kJ\ mol^{-1}}$$

DRM requires high temperatures, and at such severe conditions, catalysts are easily deactivated and carbon deposition on catalysts is unavoidable.

Recently, the utilization of an electric field has been reported to lower reaction temperatures for several catalytic reactions [2, 3]. So, we applied it to DRM reaction in order to achieve high CH_4 and CO_2 conversion even at low temperatures in an electric field over La-doped Ni/ZrO$_2$ catalysts with suppressing carbon deposition. Also, the effects of CH_4 and CO_2, and the electrical factors on DRM reaction in the electric field were investigated using various tests and characterizations.

Experimental

Catalyst-supports, 10 mol % La-ZrO$_2$ (La-ZrO$_2$) were prepared using a complex polymerized method. Then 1wt% of an active metal was loaded on the La-ZrO$_2$ support with using an impregnation method. Calcination was conducted at 973 K. The catalyst is designed as M/La-ZrO$_2$ (M = Fe, Co, Ni, Cu, Pd or Pt.)

Charge amounts of catalyst in DRM activity tests were 100 mg. In the screening tests, the feed gas was supplied at CH_4:CO_2:Ar = 1:1:2. The total flow rate was 100 mL min^{-1}. Products were analyzed using a GC-FID and a GC-TCD. The electric field was applied using a DC high-voltage power supply. Two stainless electrodes (2 mmϕ) were inserted into the reactor, with each end set as contacting the catalyst bed.

Results and discussion

In order to discover suitable catalysts for CH_4 and CO_2 conversion by DRM reaction in an electric field, various metal-supported La-ZrO_2 (10 mol % La-doped ZrO_2) oxide catalysts, M/La-ZrO_2, were investigated to assess their catalytic activities. Table 1 presents experimentally obtained results on various M/La-ZrO_2 catalysts for DRM in the electric field. The Faradaic number indicated the number of reacted molecules per electron. Increase in Faradaic number means more reactants are activated by the constant applied current. From the results in Table 1, we specifically examined the Ni/La-ZrO_2 catalyst for additional investigations considering high Faradaic number and high H_2/CO ratio.

To investigate carbon deposition on DRM reaction in the electric field, catalytic activity tests was conducted in high CH_4 conversion condition (shown in Table 2). The amount of the carbon deposits after DRM in the electric field was low thanks to the low gas phase temperature.

Table1. Catalytic activities for DRM in an electric field over M/La-ZrO_2 catalysts. [4]

Catalyst	Temp. / K	Power / W	Field Intensity / V mm^{-1}	CH_4 conv. / %	CO_2 conv. / %	CO sel. / %	CO yield / %	H_2/CO / –	Faradaic Number / –
La-ZrO_2	596	3.7	151	1.9	1.9	74.4	1.4	0.76	21
Fe/La-ZrO_2	649	3.5	228	6.9	14.6	91.2	6.3	0.23	119
Co/La-ZrO_2	619	4.5	292	20.3	31.2	99.4	20.1	0.57	252
Ni/La-ZrO_2	555	3.7	243	22.8	24.8	100	22.8	0.83	252
Cu/La-ZrO_2	626	3.9	256	3.9	3.6	88.5	3.5	0.99	42
Pd/La-ZrO_2	533	1.9	125	6.4	9.8	100	6.4	0.52	84
Pt/La-ZrO_2	580	4.1	271	21.0	23.6	100	21.0	0.80	238

Table 2. Catalytic activities and amounts of carbon deposition under a high conversion condition on DRM. [4]

		Power / W	CH_4 conv. / %	CO_2 conv. / %	CO sel. / %	CO yield / %	H_2/CO / –	Carbon deposition / mg g-cat^{-1}
no imposing EF	initial	-	63.5	52.9	100	63.5	1.20	>39.6
	140 min.	-	64.0	77.0	100	64.0	0.81	
imposing EF	initial	8.1	74.5	85.3	100	74.5	0.87	1.5
	140 min.	6.9	77.2	87.6	100	77.2	0.88	

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DESIGN OF STRUCTURED CATALYSTS FOR ETHANOL STEAM REFORMING BASED ON NANOCOMPOSITE ACTIVE COMPONENTS AND OPEN CELL FOAM SUPPORTS

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Biomass is currently considered as one of the most perspective renewable source for energy and chemicals production. Ethanol derived from biomass is the promising feedstock for hydrogen and syngas production due to its nontoxicity, easy storage and transportation. Cheap Ni-containing catalysts highly active ones in ethanol steam reforming (ESR) suffer from strong coking leading to their rapid deactivation. Coke formation could be prevented by supporting nickel on ABO_3 perovskites with a high oxygen mobility providing a high Ni dispersion and oxidation of coke precursors. Realization of ESR over heat-conducting structured catalysts improves hydrogen and syngas yield. In the previous work, catalysts based on bulk $LnFeNiO_3$ were shown to provide a high activity, stability and selectivity in ESR [1]. However, replacement of expensive lanthanides with more available raw materials is an important challenge and $CaTiO_3$ is a promising substitution of Ln-based perovskites. Another problem is a low specific surface area (SSA) of bulk perovskites and their supporting on a high SSA γ-Al_2O_3 doped by alkali-earth elements to decrease its acidity is a promising approach. In this study, the results on synthesis, structural and redox properties of catalysts based on $CaTiO_3$ (bulk and supported on 10 % Mg-γ-Al_2O_3) doped with Ni and Ru are presented. Their performance as fractions and layers loaded on open-cell foam Ni-Al-C heat-conducting substrates in ESR has been studied.

Nanocomposite active components comprised of nanoparticles of Ni(Ru) or their alloys and $CaTiO_3$ perovskite were synthesized by Pechini or citrate methods. The structural and redox properties of catalysts were characterized by XRD, BET, TEM with EDX, UV-vis, XPS, TPR-H_2. According to XRD, the phase composition of initial catalysts strongly depends on the preparation method. The single phase $CaTiO_3$ perovskite is formed only from citrate precursors. All catalysts synthesized via Pechini route along with $CaTiO_3$ contain TiO_2 admixture. The NiO reflections are observed for all bulk and supported catalysts; however, the values of its lattice parameter (***a***) suggest formation of NiO-MgO solid solution for Mg-Al_2O_3 supported samples that is confirmed by UV-vis spectra. For Pechini catalysts, a bigger ***a*** value evidences a stronger interaction of NiO and MgO. Besides, the data of H_2-TPR along with UV-vis spectra show that, in Pechini catalysts, nickel could form $NiTiO_3$-like substances due to its interaction with TiO_2 present in these samples. The data of H_2-TPR show a high oxygen reactivity in Pechini catalysts leading to reduction of Ti^{4+} in disordered TiO_2 that is confirmed by XPS data. Addition of ruthenium facilitates reduction of Ni^{2+}- and Ti^{4+}-containing species due to spillover of hydrogen activated over metal Ru formed at low temperature. For Pechini samples, a high-temperature shift of ruthenium reduction peaks in H_2-TPR spectra evidences its stronger interaction with support. TEM data for reduced catalysts show that in Pechini samples metallic particles are smaller, and some of them are decorated with TiO_x species. Decoration occurs in reducing atmosphere at high temperatures due to diffusion of partially reduced TiO_x species toward metal particles.

Catalysts testing revealed that their performance in ESR differs depending on the phase composition and $CaTiO_3$ content for supported samples. A higher activity and stability to coking are observed for catalysts prepared by Pechini route containing TiO_2 along with $CaTiO_3$. Their effective performance is due to a high dispersion of metal nickel and ruthenium particles along with promoting oxidation of carbon deposits over Me-O_V-Ti^{3+} sites. Such active sites are formed as a result of strong metal-support interaction of partially reduced TiO_x species with Ni(Ru) metal particles. The most active and stable catalyst Ni+Ru+20 % $CaTiO_3$/10 % Mg-Al_2O_3(Pechini) has shown more effective performance in ESR being loaded on the open-cell foam AlNiC support with a good thermal conductivity as compared with a ceramic substrate. Besides, it has provided higher hydrogen and CO yields than those found for $PrNi_{0.9}Ru_{0.1}O_3$/10 % Mg-Al_2O_3/AlNiC catalyst and has shown a stable performance in a realistic reaction mixture during long-term tests.

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CO-PYROLYSIS OF OIL-SLIMES AND BIOMASS

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At present, one of the significant results of anthropogenic influence on nature is the formation of a great amount of domestic and industrial wastes, particularly polymers and oil-slime, which are characterized by the stability to the natural degradation [1].

Oil-slime is bulk waste the formation of which takes place at all stages of oil production, processing and transportation. Oil-slime mainly consists of oil-products, water and mineral constituents (sand, clay, metals oxides etc.) which account for their variable composition and complicate their disposal. That is why the development of environmentally clean technology for oil- slime processing is of paramount importance [2].

The existing methods of waste processing can be divided into physical, chemical, physicochemical, thermal and biological [1]. The choice of the waste processing method mostly depends on the amount and nature of organic compound in waste.

Nowadays great attention is paid to the search of the methods of the increase of pyrolysis process effectiveness to raise the yield of liquid and gaseous products. For this purpose different catalysts such as Ni chlorides and nitrates, alkali and alkaline-earth metal oxides and carbonates, cuprum salts, zeolites are widely used [3].

The study of the pyrolysis process was conducted at varying the temperature in the range of 400-600 °C and catalyst concentration. Catalytic efficiency was estimated considering the total amount of the gaseous mixture produced during pyrolysis, the concentration of hydrocarbons (methane, ethane, ethylene, propane) in gaseous mixtures and the heat of combustion of combustible gases.

The natural aluminosilicates (kaolin, bentonite) and synthetic zeolites (cambrian clay and clay mergel marked as H-Beta-25 and H-Mord) were purchased from Zeolyst International, USA. It is important to mention that zeolite catalysts were modified with Fe using repeated ion exchange (the iron precursor is ferric nitrate). Both natural aluminosilicates and synthetic zeolites were used as the catalysts for low-temperature pyrolysis of peat.

The pyrolysis process was carried out using an experimental pyrolysis set-up in a temperature range from 450 to 650 °C. The experimental pyrolysis set-up consists of a metal fixed-bed reactor heated with the electric furnace, a gas sampler, a water trap for collecting liquids, and a eudiometer for collecting gas.

The use of co-pyrolysis of peat, polymeric waste and oil-containing waste allows increasing considerably the rate of pyrolysis processes with the production of gaseous and liquid fuels. The search of the catalytic system for the co-pyrolysis processes of organic raw materials demands an individual approach in each case.

Co-pyrolysis of peat and oil-slime in the presence of bentonite clay resulted in the increase of the yield of gaseous products from 18 up to 26 % wt., and liquid fraction – from 45 up to 55% wt. Besides, the higher yield of C1 – C3 hydrocarbons (up to 10 – 20 %) was observed.

The use of metal chlorides of iron subgroup (2 % wt. concentration) at 500 °C in the process of co-pyrolysis of peat and polymeric waste resulted in the optimal conversion of the substrate in desired products. A total weight of gaseous and liquid products was increased up to 15 %, and at the same time the amount of char decreased.

Thus we have found that the use of catalytic systems does not only decrease the pyrolysis temperature but intensifies the processes of refining and ennobling of low-grade natural raw material.

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OP-II-9

A DUAL-BED CATALYST SYSTEM FOR ULSD PRODUCTION FROM THE MIXTURE OF RAPESEED OIL AND SRGO

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The growing demand in transportation fuels, decrease in available fossil fuel resources and vital tendency to reduce the greenhouse gas emissions have caused ascending interest in the involvement of renewable feeds for their production. Hydrotreating of the triglyceride-based feedstocks gives linear hydrocarbons which are the excellent components of diesel-range fuels being fully compatible with the petroleum-derived products and having the improved cetane number, gravity, aromatic and sulfur contents. The critical challenge in the developing of the new energy-efficient co-processing of the triglyceride-based feedstock with the straight–run gas oil (SRGO) for ULSD (ultra-low sulfur diesel) production is the elucidation of peculiarities of sulphide catalyst's behaviour depending on their chemical composition.

Comparative study of sulfide Mo/Al_2O_3, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts have been performed with the emphases on the 1) pathways of aliphatic ether transformation during hydrotreating using methylpalmitate (MP) as model compound and rapeseed oil (RSO), 2) rapeseed oil effects on SRGO hydrotreating. As a result, dual- bed catalytic system is proposed for the effective co-processing of rapeseed oil – straight-run gas oil into ULSD.

The catalysts are prepared by impregnation of alumina extrudates with a solution of active metals precursors, phosphoric and citric acids. The hydroprocessing of MP, RSO, SRGO and blended feeds was carried out in trickle-bed reactor at 3.5-7.0 MPa, 300-360 °C, LHSV 1-2 h^{-1}, H_2/feed ratio 300-1000. The liquid and gases products were quantified using gas chromatographs, ANTEK 9000NS and Vario EL Cube were used to follow total S, N and O contents. The quality of produced fuels was checked using the corresponding ASTM methods. Characterization of the catalysts in the sulfide state by means of XPS, XRD and HRTEM confirmed that the applied preparation and sulfidation procedures provide the formation of highly dispersed MoS_2, CoMoS and NiMoS nanoparticles (3-5 nm) on the alumina surface.

It was observed, that hydrodeoxygenation of MP and RSO over $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts occurs via both pathways: direct HDO producing hydrocarbon and H_2O and decarbonylation/decarboxylation with formation of hydrocarbon with shorter chain and carbon oxides (CO/CO_2). On the contrary, the un-promoted MoS_2/Al_2O_3 catalyst turns the reaction to HDO route, avoiding the formation CO/CO_2 molecules. The comparison of catalyst's performance in RSO-SRGO blends hydrotreatment let us to conclude, that an addition of rapeseed oil (5-15 wt %) inhibits the HDS and HDN activities of $CoMo/Al_2O_3$ catalyst, whereas activities of $NiMo/Al_2O_3$ catalyst are not affected. In accordance, over $NiMoS/Al_2O_3$ catalyst ULSD can be produced from SRGO and RSO-SRGO blend at the same conditions, whereas the temperature increase is needed if the $CoMoS/Al_2O_3$ catalyst is used for ULSD production from RSO-SRGO blends. It was observed that addition of CO (by-products of RSO conversion) to the hydrogen flow had the same effect on the HDS and HDN activities of the sulfide $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts as the addition of RSO to the SRGO feed. Carbon monoxide is proposed to be the main inhibitor of sulfide $CoMo/Al_2O_3$ catalyst's activity. This assumption was supported by the observation that addition of benzofuran giving only water in HDO reaction had a minor influence on the activity of sulfide $CoMo/Al_2O_3$ catalyst in HDS of SRGO. Taking into account the discovered peculiarities the dual-bed catalytic system was proposed for the hydrotreating of RSO-SRGO mixture. The use of sulfide Mo/Al_2O_3 catalyst in the front layer for the RSO conversion diminished the CO_x formation and allowed to use the sulfide $CoMo/Al_2O_3$ catalyst in the second layer without significant decrease of HDS activity. Absence of CO_x in the gas phase gives one some technological advantages: CH_4 formation through CO_x hydrogenation is escaped and necessity of costly and energy-intensive purification of recycle hydrogen in co-processing of RSO-SRGO mixtures is avoided.

Acknowledgements

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OP-II-10

CO-FEEDING PYROLYSIS LIQUIDS WITH CRUDE OIL DISTILLATES IN FCC UNIT

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FCC co-processing of bio-liquids as pyrolysis oils seems one of the best solutions to produce 2G biofuels. Advantageously, it avoids dedicated blending infrastructure and blend wall limits (such as in place for ethanol in gasoline). In this presentation, an overview is given on the latest results of co-feeding pyrolysis liquids (and those hydrotreated) in FCC units, with specific emphasis on catalyst development and experimental results. Results will be compared with alternative 2G biofuel production routes as lignocellulosic ethanol and the Fischer-Tropsch on biomass derived syngas.

1. Scope

Fluid Catalytic Cracking (FCC) is one the most important conversion process used in petroleum refineries, and up to 1/3 of the refinery's heavy petroleum feedstock goes through such a unit. Its principal aim is to convert high molecular weight hydrocarbons obtained from crude oil distillation into more valuable product, mainly gasolines. To meet Europe's renewable energy targets by 2020 (up to 10 % share in all forms of transport fuels) a realistic alternative to the first generation bio-fuels is to produce hybrid bio- and fossil FCC fuels by co-refining with pyrolysis liquids in a conventional oil refinery. In this way FCC co-processing is one of the best solutions, fully controlled by the refiner, allowing the production of renewable gasoline & diesel-like hybrid stocks and generation of lignocellulosic derived fuels. Advantageously, it avoids dedicated blending infrastructure and blend wall limits (such as in place for ethanol in gasoline). The potential of that process has recently been demonstrated by Petrobras/NREL, and further confirmed by Ensyn / UOP, both to produce renewable gasoline and diesel. In this presentation, an overview is given on the latest results of co-feeding pyrolysis liquids (and those hydrotreated) in FCC units, with specific emphasis on catalyst development and experimental results. Results will be compared with alternative 2G biofuel production routes as lignocellulosic ethanol and the Fischer Tropsch on biomass derived syngas.

2. Results and discussion

In the European project FP6 BIOCOUP, the proof of principle studies that upgraded pyrolysis liquids could be well treated in existing FCC units was demonstrated, and these results are detailed in the FP7 NMP project FASTCARD where improved catalysts are being developed to be used in the full chain of co-FCC processing pyrolysis liquids, and in which links between bio-liquids upgrading and co-FCC performances have been identified. Co-refining of bio-oils in a Fluid Catalytic Cracking (FCC) unit leads to changes in the product quality, such as a higher aromaticity and the presence of residual (phenolic) oxygenates as well as an increased coke content of the FCC catalysts. However, to preserve naphtha yield and quality while avoiding excessive coke production, a pyrolysis liquid upgrading process can be deployed prior to the co-processing step. The upgrading processes are based on a hydrotreatment step, aiming to reduce the number of oxygen functionalities in the pyrolysis liquid (to render a ‘stabilized oil’) or to substantially remove the oxygen to render a lean fuel (‘deoxygenated oil’).

In both cases the liquids are less prone for charring. Interestingly an optimum might exist between hydrogen consumption and degree of deoxygenation of pyrolysis liquids on the one hand, and overall product yield/quality on the other hand. Pyrolysis liquids as such can successfully be co-fed in FCC, however, it proceeds at the expense of overall biomass-to-fuel carbon yield, opposed to mildly treated liquids.

Co-FCC performance is investigated as a function of the hydrotreatment severity of the pyrolysis liquids over a newly developed Picula^{TM} catalyst, developed in a collaboration between BTG and BIC. Untreated PO sample was completely immiscible with VGO and could not be processed in the MAT unit and therefore no results are presented for this test. The tests were conducted at low and high cat/oil ratios to investigate the impact of the conversion on the selectivity, all at a blend level of 10 wt. % pyrolysis liquid with 90 wt. % fossil feed. Figure 1 reports changes in the conversion and naphta yield as a function of the amount of hydrogen consumed for the PL upgrading. The dotted lines correspond to FCC of 100 wt. % VGO feed. [1]

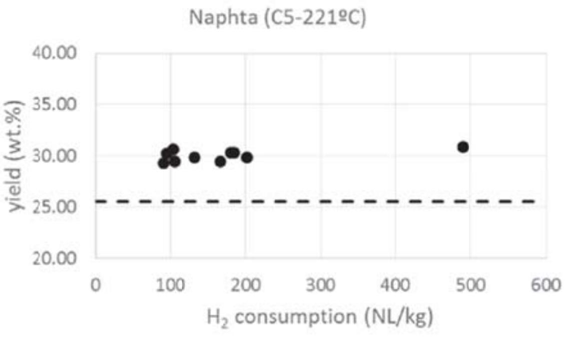

Figure 1. Typical yields of the naphta fraction in an FCC of 10 wt. % PL and 90 wt. % VGO co-processing as a function of H_2 consumption measured during PL upgrading

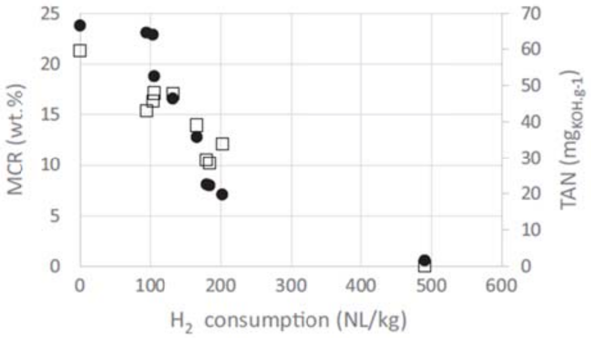

Figure 2. Evolution of the MCR (black circles) and TAN (empty squares) as a function of the H_2 consumption during the upgrading treatment of the initial pyrolysis liquid

The better performance of treated liquids compared to pure pyrolysis liquids can be understood by a dramatic change in the liquid's characteristics (MCRT, TAN, hydrogen to carbon ratio (H/C), oxygen to carbon ratio (O/C) and water content) once treated. Most relevant for FCC processing are the MCRT and TAN, and these are plotted as a function of the hydrogen consumption during the upgrading step in Figure 2. Notwithstanding a much lower water content than the untreated pyrolysis liquids, a strong decrease in the MCRT and TAN is noted. The MCRT goes from 24 wt. % for PL down to 15 wt. % for products obtained at 160 °C (100 L/kg$_{PL}$), and a further strong reduction <10 wt. % above 220 °C (>150 NL/kg$_{PL}$). Similar trends are shown for the acidity (TAN). The rather high and stable value of MCR for these pyrolysis oil samples upgraded under mild conditions correlate with the coke-forming tendency as will be revealed in the FCC co-processing section. For the more severe upgrading conditions, up to the fully deoxygenated RO sample, the values of MRCT and TAN are reduced drastically, clearly revealing a major change in the chemistry in this second part of the hydrogen consumption range.

3. Conclusions

The co-refining applied to FCC is a process that can be considered as a compliance solution controlled by the refiner, allowing to produce and track renewable naphtha stocks. Several studies have demonstrated its feasibility, both at lab and pilot scale, and in this study we have determined how the severity of the upgrading step influences the quantity and quality of the co-FCC products in a lab MAT unit. A slightly higher quantity of naphtha than that for pure VGO cracking was observed during co-processing, independently of the upgrading severity. On the other hand, higher coke yields during co-processing were obtained that decreased with increasing upgrading severity. Similar coke levels as those for pure VGO cracking were obtained at hydrogen upgrading consumptions >150 NL/kg$_{PL}$. An optimum in the naphtha yield and quality in terms of RON, MON, and PIONA was found for the mildly hydrotreated pyrolysis liquids already, corresponding to an acceptable level for the H_2 consumption.

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OP-II-11

PHOTOCATALYTIC NANO-HYBRID SYSTEM FOR H_2 PRODUCTION

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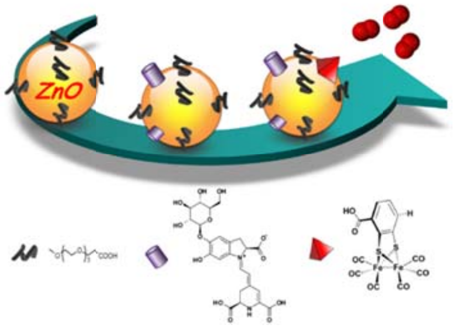
Solar energy plays an important role both in the generation of electricity and flues. Conceptually artificial photosynthesis [1] converts photons into chemical bonds, and can be attained by a plethora of concepts and strategies. The most promising technologies employ semiconductors to attain robust large-scale solar energy production devices. ZnO is an eligible system however its amphoteric nature precludes usage in aqueous media. The use of polymers, for stabilization and transfer of semiconducting nanostructures to water is an option to overcome these impediments [2]. The combination of molecular sensitizers, capable of absorbing solar light, and molecular proton reduction catalysts, both attached to the semiconductor enhances this strategy.

Water-soluble ZnO NCs were prepared according to the recently developed organometallic synthetic approach and fully characterized by UV-Vis, DLS, HRTEM, PXRD methods [3]. The modification of ZnO with 2,5,8,11-tetraoxatetra-decan-14-oic acid (OEG) has extended the electrons lifetime in the CB to seconds. This is several orders of magnitude from what has been published with other oxides, opening prospectus for photovoltaic applications but more importantly for photocatalysis reactions.



Scheme 1. Schematic representation of ZnO-OEG NCs functionalization with betanin *(purple cylinder)* and catalyst *(red pyramid)*

We created a nano-hybrid system for H_2 evolution under visible light irradiation, schematically depicted in scheme 1 [4]. Light harvesting was undertaken by a natural molecular dye (betanin) extracted from beetroot, capable of injecting up to two electrons per photon absorbed into ZnO conduction band in less than 15 ps. As H_2 evolving catalyst, we opted for the [FeFe](mcbdt)$(CO)_6$ (mcbdt = 3-carboxybenzene-1,2-dithiolate) catalyst, a molecular mimic of [FeFe]-hydrogenases. UV-Vis and FTIR measurements verified, what betanin [B] and the catalyst [Cat] were covalently tethered to the exposed ZnO surface via the carboxylic anchoring groups.

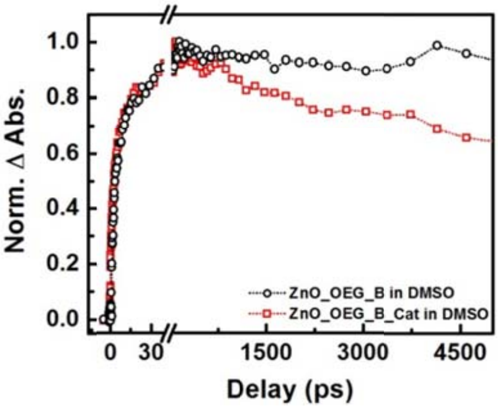


Fig. 1. Kinetic traces at 1897 cm^{-1} extracted from transient mid-infrared absorption spectra collected from 1850-2200 cm^{-1} of ZnO-OEG-B and ZnO-OEG-B-Cat NCs upon excitation at 530 nm in DMSO

Ultrafast transient mid-infrared absorption spectroscopy measurements were performed to confirm electronic connection between sensitizer and catalysts modulated by the semiconductor. It was shown that betanin electron injection into ZnO-OEG occurs at two distinct times upon excitation at 532 nm, similar for both systems with and without catalyst. However, the presence of molecular catalyst led to an almost immediate drop in infrared absorption after electron injection, indicative of fast and effective transference of electrons from the ZnO-OEG-B to the molecular iron catalyst.

Photocatalytic production of H_2 was evaluated on a purposely-built flow photoreactor with CW laser (532 nm) and QMS as gas product detection [5].

In conclusion, we reported the first ultra-stable and water-soluble carboxylate oligoethylene glycol functionalized ZnO nanocrystals with slow back electron transfer dynamics (up to microseconds), which is related to hole stabilization. The material is a core shell system with an almost impermeable OEG that can however be sensitized a posteriori (required to shift material light absorption to the visible range). The properties of ZnO-OEG NCs circumvent all the known disadvantages, which precluded its large-scale use in n type solar applications. The novel nano-hybrid H_2 evolution system efficacy is intimately connected to the ZnO-OEG.

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FCC OF UPGRADED PYROLYSIS LIQUIDS MIXED WITH CRUDE OIL DISTILLATES: COMBINED STRATEGIES FOR IMPROVING BIO-FUELS YIELDS AND QUALITY

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In order to meet the EU's renewable energy targets by 2020 (up to 10 % share in all forms of transportation fuels[1]), a realistic alternative to first generation bio-fuels is to produce hybrid bio/fossil fuels by co-refining biomass pyrolysis liquids (PL) with crude oil fractions in a conventional oil refinery[2]. However, co-refining may lead to severe changes in products quality, such as a higher aromaticity and residual oxygenates in the hybrid fuels that are produced. For the case of co-FCC (fluid catalytic cracking), various strategies can be implemented to limit those impacts along this complex value chain ranging from bio-mass to bio-gasoline.

A first strategy was tested to preserve the gasoline yield and quality by implementing a PL hydrotreating prior to co-processing, to lower their oxygen content[3]. By following the changes in conversion, yields and gasoline composition (aromatics/olefins vs saturated alkanes) as a function of the bio-oils hydrotreating severity, measured in a Micro Activity Test (MAT) reactor, it was shown that a compromise could be reached between bio-oil upgrading severity and FCC products yields and quality (RON, PIONA analysis). An optimum in the gasoline yields and quality was found by adding 10 to 25 wt. % of a mildly deoxygenated bio-oil to a standard VGO, via a co-processing carried out on a commercial equilibrated FCC catalyst.

A second strategy was to adapt the FCC catalysts to the presence of oxygenate molecules typical of the bio-feedstock still present in the upgraded pyrolytic liquids. To that end, Y zeolites, which are the main active component in FCC catalysts, were upgraded by creating a mesoporosity in addition to the microporosity to favor the diffusion of the large lignocellulosic fragments throughout the cracking catalysts, according various hierarchical post synthesis processes[4,5].

Samples	V_{meso}[a] ($cm^3 \cdot g^{-1}$)	V_{micro}[a] ($cm^3 \cdot g^{-1}$)	S_{BET}[b] ($m^2 \cdot g^{-1}$)
HY_0	0	0.23	830
HY_1	0.27	0.17	791
HY_2	0.50	0.08	780

Table 1. Changes in porosity from the HY_0 (unprocessed), HY_1 and HY_2, post processed according [4] and [5], respectively

Table1 shows how a microporous HY_0 zeolite (from ZEOLIST) can be post-processed for generating a controlled mesoporosity such as HY_1, mixed micro-meso-porous, and HY_2, mostly mesoporous.

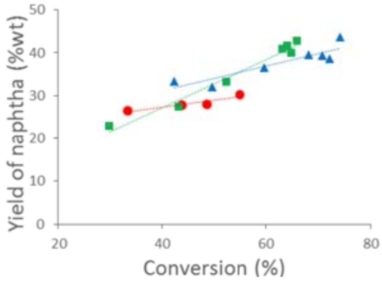

Figure 1. Naphta yields vs conversion under co-processing conditions (10 % of mildly hydrotreated pyrolytic bio-oil and 90 % VGO)

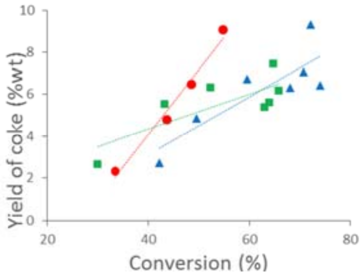

Figure 2. Coke yields vs conversion under co-processing conditions

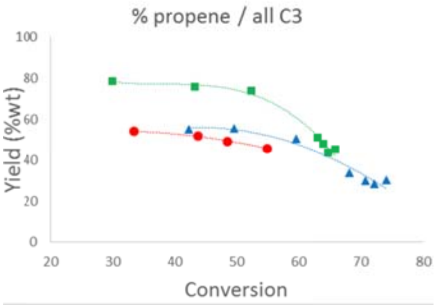

Figure 3. Olefinic fraction for C_3 products vs conversion under co-processing conditions

The main effects of replacing progressively micro- by meso-porosity are i) to slightly increase naphta yields (Fig. 1), ii) to decrease coke formation at high conversion (Fig. 2), iii) to increase the unsaturated fraction in gaseous (C3-C5) (Fig. 3) and liquid products (not shown here), and iv) to decrease markedly the remaining oxygenated products in the liquid fraction (mainly alcohols, acids and phenolics, from ^{31}PNMR measurements). These effects underline the positive role of creating a mesoporosity in hierarchical FCC catalysts, in line with cracking mechanistic features.

The combined impact for these two strategies on co-FCC will be discussed as a guideline for minimizing the cost of bio-oils upgrading and thereof the hybrid transportation fuels, while maintaining their quality within the specification limits.

Acknowledgements

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STRUCTURE FEATURES OF Mo-BASED DISPERSED CATALYSTS IN HYDROCRACKING AND STEAM CRACKING OF HEAVY OIL

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Recently, the number of publications describing thermal and thermocatalytic transformations of heavy hydrocarbon feedstocks (HHCF) in the presence of water (steam cracking) has been steadily growing. Such feedstocks are characterized by high viscosity, high content of sulfur and metals, large amount of asphalt-resinous components and small amount of light hydrocarbon fractions. These processes lead to reduced viscosity, improved hydrocarbon composition and reduced content of heteroatoms in the resulting products [1-3]. The use of catalysts in the steam cracking processes allows one to increase the efficiency of HHCF thermal transformations and consequently increase the quality of semisynthetic and/or synthetic oil. Mo-containing catalysts are widely used in traditional hydrotreatment processes [4]. The effectiveness of molybdenum-containing ultra-dispersed catalyst has been demonstrated in hydrocracking of heavy hydrocarbon feedstocks at elevated hydrogen pressures (6-7 MPa) [5]. The dispersed nature of the catalyst thus prepared reduces mass transfer limitations and blocking of pores by coke deposits, which is typical of traditional heterogeneous catalysts.

The aim of the present study was to investigate the structure features of Mo-based dispersed catalysts in hydrocracking and catalytic steam cracking of high-sulfuric heavy oil (HO) (Tatarstan, Russia).

The experiments were carried out in a batch reactor at 425 °C for 1 hour, catalyst concentration 2.0 wt. %, water to feedstock ratio (wt) 0.3:1. Catalytic steam cracking (CSC), catalytic cracking in the absence of water (CC) and hydrocracking (HC) processes were carried out. The aim was to study the effect of water, the presence of the catalyst and the process conditions on composition and properties of HO conversion products, structure features of catalysts. The evaluation of processes effectiveness was performed using the yields of light fractions (b.t. < 350 °C), synthetic oil (b.t. < 500 °C), semisynthetic oil (total liquid product), coke and gaseous products. In addition, the H:C atomic ratio, sulfur content, density and viscosity were estimated. Solid products (coke) containing catalyst were investigated by HRTEM, XRD and XANES/EXAFS.

It was shown that CSC of heavy oil in the presence of dispersed Mo-containing catalyst at 425 °C produced low viscous semisynthetic oil with higher H:C ratio, as compared to CC processes. It was observed that water during CSC process promoted desulfurization with intense formation of sulfur-containing gaseous products. The H:C ratio of the liquid products increased as well from 1.62 to 1.70.

Based on the properties of products, the processes complied the following order: HC > CSC > CC without water. When the process was carried out at optimal conditions (425 °C, 1 h), the yield of light fractions was the same for both CSC and HC processes (51 wt. %). The liquid products of the catalytic steam cracking meet all the requirements established to semisynthetic oils to be transported by oil pipelines to oil refinery. It was found that the CSC process in the presence of Mo-containing catalysts could potentially be applied to HHCF pre-processing into semisynthetic oil directly at the oil field. Besides, the advantage of this process is that it does not require the hydrogen supply.

According to HRTEM and XRD study of solid products, the active component of the catalyst is presented by MoS_2 and MoO_2 phases. The composition and properties of MoS_2 phase depend on the reaction conditions of thermal catalytic conversion of heavy oil (the use of steam or H_2). The local surrounding of atoms in dispersed catalytic systems was studied by XANES/EXAFS. It was shown that Mo-containing component was in the form of MoO_2, MoO_3, and MoS_2 in the solid residue (coke) after catalytic steam cracking at 425 °C. Based on XANES data, the content of these phases was 74 %, 10 % and 16 %, respectively. In the case of catalytic cracking without water this solid residue contains the active component preferably in the form of MoS_2 (63 %) and MoO_2 (37 %). For hydrocracking process the registered forms were MoS_2 (75 %), MoO_2 (19 %) and MoO_3 (6 %).

Thus, catalytic steam cracking process is promising for heavy oil upgrading. The structure features of active component of Mo-based dispersed catalysts depend on the reaction conditions of thermal catalytic conversion of heavy oil (the use of steam or hydrogen).

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Acknowledgements

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ORAL PRESENTATIONS

Section III. CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions
Catalytic approaches for the processing of pyrolysis biomass products
Conversion of carbon rich unconventional fossil resources and biomass feedstock into biofuel

CATALYTIC EFFECT OF CaO AND $Fe_2(SO_4)_3$ ON THE PYROLYSIS OF CASSAVA WASTE

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Nowadays, catalytic pyrolysis is a promising technology that no use hydrogen, and can be achieved at atmospheric pressure [1]. In the other hand, important amounts of residues are generated during the processing of starch from cassava. We studied the effect of $Fe_2(SO_4)_3$ and CaO on the kinetics of the pyrolysis reaction of cassava industrial wastes, as an approximation to generate options to exploit this material. Mixtures of cassava industrial wastes with 3 %w of the selected catalysts were analyzed in a thermobalance under He atmosphere at heating rates of 10, 30, and 100 K/min. Kinetics parameters were obtained fitting data to three kinetic models: differential isothermal, integral isoconversional [2, 3], and distributed activation energy models with Gaussian normal distribution coded in Matlab [4, 5]. DTG curves were qualitatively compared and results showed a marked influence on DTG profile, of the catalysts employed (figure 1). The DAEM model with three sets of reactions showed to fit better to experimental data than the others explored models (figure 2). Regressed kinetics parameters showed a higher influence of $Fe_2(SO_4)_3$ on pyrolysis of cassava waste in accordance with DTG qualitative interpretation, when compared to CaO, the mixture of $Fe_2(SO_4)_3$ and CaO, and the influence of the heating rate. Results suggest a change of reaction mechanism with the heating rate and the presence of both catalysts.

OP-III-1

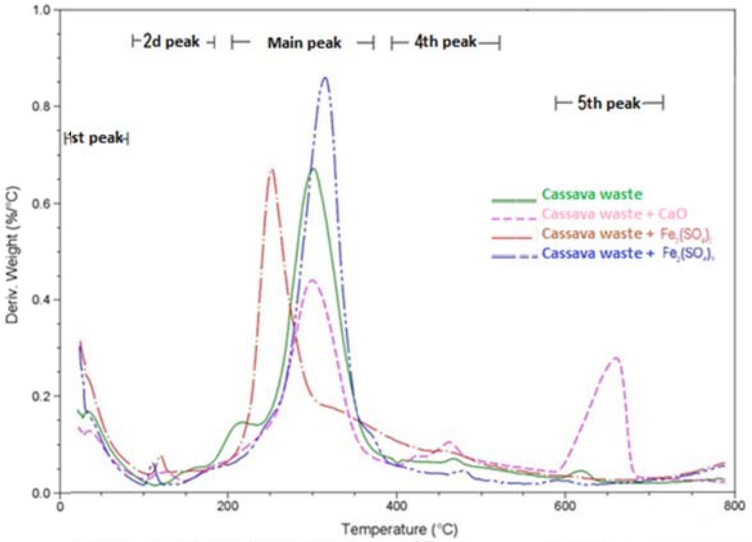

Figure 1. DTG curves of cassava industrial waste with and without catalysts at 10 K/min

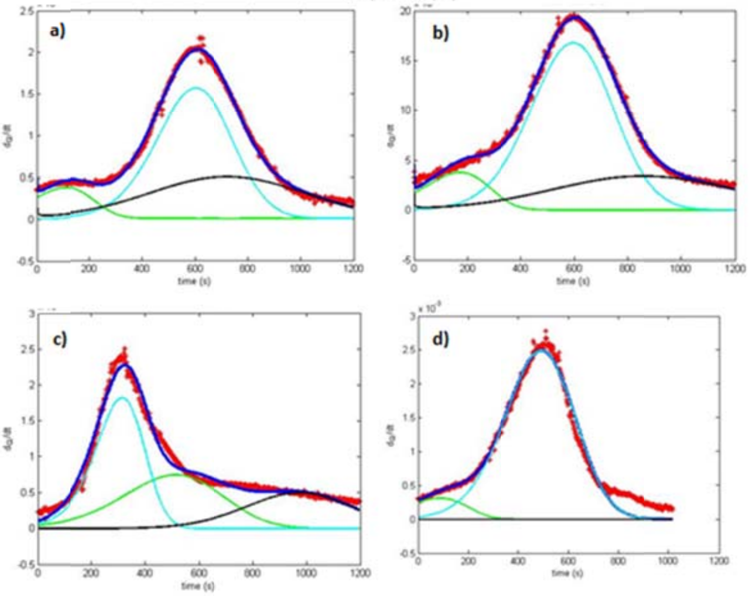

Figure 2. Fitting to DAEM model. Heating rate: 10 K/min.
a) Cassava waste
b) Cassava waste + CaO
c) Cassava waste + Fe$_2$(SO$_4$)$_3$
d) Cassava waste + CaO + Fe$_2$(SO$_4$)$_3$

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Acknowledgements

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METAL OXIDE PROMOTED Pt/Al_2O_3 CATALYSTS FOR NON-EDIBLE OIL-DERIVED 2nd GENERATION BIOFUELS

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Abstract. We report here, for the first time, the application of group 6 and 7 metal oxides (MoO_x, WO_x and ReO_x) promoted Pt/Al_2O_3 catalysts for deoxygenation of fatty acids/non-edible jatropha oil producing diesel-range hydrocarbon. These bimetallic catalysts exhibited enhanced catalytic activity and selectivity for hydrodeoxygenation than the unpromoted catalyst. Near complete conversion of fatty acids/vegetable oils to hydrocarbons was achieved at 260 °C and at low hydrogen pressures (1-5 bar). The catalyst was reusable. Metal dispersion and synergy between Pt and metal oxide are the possible causes for the enhanced catalytic activity of these promoted Pt catalysts.

Introduction. With depleting fossil fuel resources and increasing concerns about the environment, renewable fuels have been gaining importance. Biofuels are an important component of renewable fuels. Diesel-range hydrocarbons (2nd generation biofuels) produced by hydrotreating of non-edible oils can be used directly as fuel in the conventional diesel engines [1]. Common hydrotreating catalysts (Mo or W-promoted Ni or Co/Al_2O_3) require high temperatures and hydrogen pressures. It is desirable to develop a highly stable, active and selective catalyst that operates at moderate conditions. Recently, we reported the application of Pt-WO_x/$AlPO_4$-5 catalyst for this conversion. While it is highly active and selective for hydrodeoxygenation, the support lost its integrity on use [2]. We report here, the catalytic application of group 6 and 7 metal oxides promoted Pt/Al_2O_3 for deoxygenation of fatty acids/non-edible oils. The metal oxides acted as structural and electronic modifiers of Pt enhancing its catalytic performance.

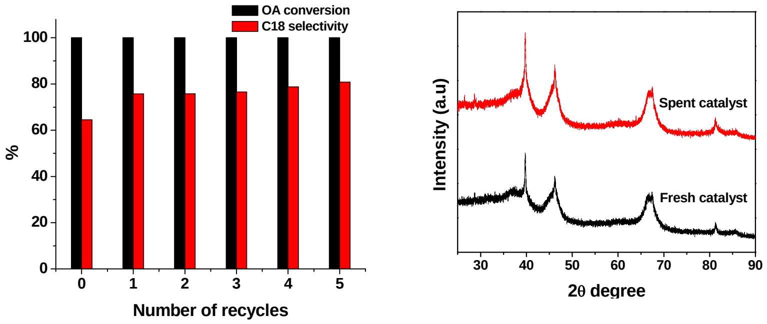
Experimental. Catalysts were prepared by wet impregnation method followed by calcination (@450 °C, 4 h) and reduction (@350 °C, 150 min). They were designated as xPt-yMO_x/Al_2O_3 where x and y refer to Pt and group 6 and 7 metal wt %, respectively. They were characterized by several physicochemical techniques. Reactions were done in 300 ml Parr stainless steel pressure reactor. Products were analyzed by GC and confirmed by GC-MS.

Results and discussion. Heptadecane (formed by decarbonylation/ decarboxylation of oleic acid, OA) is the main product (79 % selectivity at 76 % OA converison) over 4Pt/Al_2O_3 catalyst at 320 °C, 20 bar H_2 and 5 h. On the contrary octadecane (formed by hydrodeoxygenation of OA) is the major product (67.1 % at 100 % conversion) over 4Pt-8WO_x/Al_2O_3 catalyst under similar reaction conditions. The influence of temperaure and H_2 pressure have been investigated. OA conversion of 95 % was observed at 260 °C. Reaction occurred even at 1 bar hydrogen pressure. Table 1 lists the activity data of these catalysts. Figure 1 (left) depicts the stability of the catalysts in 5 recycling experiments. XRD and TEM pointed out the structural integrity of the spent catalysts (Figure 1, middle and right). Details on the influence of other oxides on activity of Pt was also studied.

Table 1. Catalytic activity of WO_x-promoted Pt/Al_2O_3 in hydrotreating of oleic acid

Catalyst	OA conversion (mol %)	Products selectivity (%)			
		C_{18}	C_{17}	$C_{10\text{-}16}$	Others
4Pt/Al_2O_3	76.0	19.0	79.0	1.2	0.4
4Pt-8WO_x/Al_2O_3	100	67.1	31.6	1.3	0

Reaction conditions: OA = 2 g, n-heptane (solvent) = 30 g, catalyst = 10 wt % of OA, 20 bar H_2, T = 320 °C, t = 5 h.



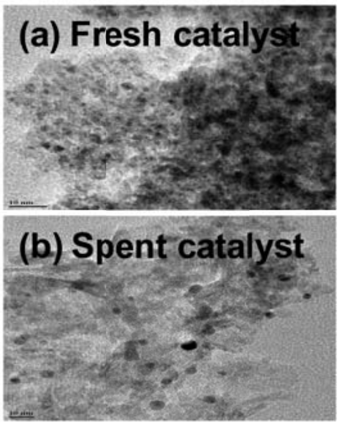


Figure 1. Left: Reusability, middle: XRD characterization and right: TEM images of 4Pt-8WO_x/Al_2O_3 catalyst

WO_x enhanced the acidity, increased the particle size of Pt and enhanced the redox behavior. This synergy between Pt and metal oxide is the cause of the high activity and selectivity of supported Pt. Also the strong support-Pt interaction is the cause of the high stability in reusability studies.

Conclusions. Group 6 and 7 metal oxides enhance the catalytic performance and hydrodeoxygenation selectivity of Pt/Al_2O_3. The catalyst was stable and reusable.

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BIODIESEL PRODUCTION METHODS

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Due to the shortage of oil reserves as well as low level of its refining (85 %) in European countries [3], there is a need for creating technologies and production of alternative types of fuel. However, biodiesel is one of the most popular types of fuel, since the transport with diesel engines accounts for more than half of all vehicles.

In Russia, use of diesel cars is lower than in Europe but this means of transport gains popularity due to advantages of the fuel such as improved ecological properties (reduction of hydrocarbon, disperse particles, volatile organic compounds emission into the atmosphere when diesel fuel is combusted in a car engine [2]), advanced lubricating property, increased cetane rating, using renewable feedstocks.

There are several methods of production of eco-friendly biodiesel: esterification of fats and fatty acids, interesterification of lipids and oils, etc.

The process of esterification of fatty acids contained in oils (for example, sunflower, corn and flax-seed) and animal feed (fish liver oil) gained the greatest popularity. This technology is a reaction of organic acids and alcohols interaction with receipt of esters. The scheme is shown at Figure 1 [1].

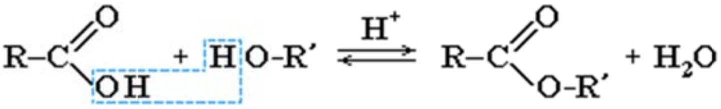

Fig. 1. Scheme of esterification reaction

The authors selected the following types of raw material to obtain biodiesel by this method: acids contained in sunflower oil and diatomic alcohol (ethylene glycol). After esterification there was phase separation (ethereal and water) by desilting, drying and distilling.

Table 1. Physical and chemical parameters of biodiesel after esterification

Property	Units	Fatty acids	Ester
Density under 20 °C	kg/m^3	0.90978	0.91400
Viscosity under 40 °C	mm^2/s	27.995	23.25
Flash point tempearture	°C	115	110
Sulfur content	mg/kg	13	71
Lubricating property: corrected WSD	μm	157	202

Table 1 presents main properties of biodiesel obtained by esterification reaction of sunflower oil and diatomic alcohol compared to physical and chemical parameters of fatty acids obtained from oil.

One more popular method of biodiesel production is interesterification of agricultural oils – a chemical exchange reaction of fat structural elements (Figure 2). In the process of interesterification molecular composition of triglycerides is changed, so physical and chemical characteristics of the product are varied as well.

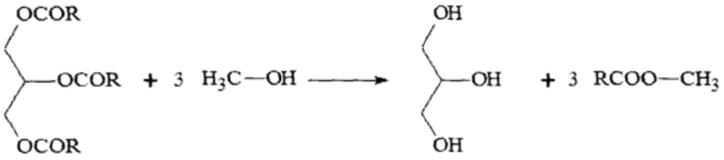

Fig. 2. Scheme of agricultural oils interesterification [4]

Standard butyl alcohol was used for interesterification to get esters as well as cameline, flax-seed, corn oils. Sulphuric acid was a catalyzator.

Table 2. Physical and chemical parameters of oil seed esters

Property	Units	n-BERM[1]	n-BELM[2]	n-BEKM[3]
Density under 20 °C	kg/m^3	0.87659	0.8700	0.8758
Viscosity under 40 °C	mm^2/s	4.5719	5.0	4.492
Flash point tempearture	°C	150	135	120
Sulfur content	mg/kg	5.5	6.8	8.51
Cetane rating		56	53	51
Lubricating property: corrected WSD	μm	553	601	592

Table 2 presents main physical and chemical characteristics of obtained fuels. Cameline oil is the best raw material for obtaining biodiesel by interesterification, since it has lowest sulfur content (5.5 ppm), largest flash point temperature (150 °C), highest cetane rating (56) as well as lowest Wear Scar Diameter (553 μm).

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[1] normal butyl ether of cameline oil
[2] normal butyl ether of flax-seed oil
[3] normal butyl ether of corn oil

OP-III-4

PRODUCTION OF DIESEL FUEL BLENDING COMPONENTS FROM WASTE AND CONVENTIONAL SOURCES

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The development and application of bio- and alternative fuels are especially important tasks nowadays. Numerous factors justify this e.g. protection of environment and human health, achieve sustainable development, increase economic growth, create new jobs, etc. Diesel fuel is especially important in the European Union (EU), its global demand will be also increased in the future. The ratio of diesel + jet fuel demand to that of gasoline is expected to increase to around 2.4 by 2040 [1]. According to this fact, it is necessary to develop bio- and alternative fuels, which are capable to operate Diesel engines.

The widely used biodiesel (fatty acid alkyl esters) has a lot of disadvantages (e.g. low thermal and oxidation stability, bad cold flow properties, lower energy content etc.) and mainly produced from vegetable oils [2]. That is why, the EU will limit and decrease the use of food-based fuels to avoid the endangering of cultivation of food and feed crops. The maximum share of food-based biofuels will be decreased to 3.8 % by 2030. Moreover, the share of renewable and low-carbon fuels should be increased to 6.8 % (included at least 3.6 % advanced biofuel) by 2030, too [3].

Based on the aforementioned reasons, the aim of our research work was to investigate catalytic hydrogenation of blends of gas oil fraction from thermal cracking of waste polypropylene (PPGO) (5-30 %), waste cooking oil (WCO) (20-45 %) and unrefined gas oil fraction (GO) (50 %) on a $NiMo/Al_2O_3$ catalyst in sulphided state to produce diesel fuel. The effects of feed compositions and process parameters [temperature, liquid hourly space velocity (LHSV)] on the quantity and quality of the main products were investigated. The applied process parameters were the following: $T = 300\text{-}360$ °C, $LSHV = 1.0\text{-}3.0\ h^{-1}$, $P = 40$ bar, hydrogen/feedstock ratio = 400 Nm^3/m^3.

Based on the experimental results we concluded that good quality diesel fuel blending components can be produced from feedstocks containing 20-30 % PPGO, 20-30 % WCO, 50 % GO, when favourable process parameters (P = 40 bar,

$T = 360\ °C$, LSHV = $1.0\ h^{-1}$, hydrogen/feedstock ratio = $400\ Nm^3/m^3$) and sulphidated NiMo/Al_2O_3 catalyst are applied. The products contain high amount of waste derived components (approx. 50 %) from different sources.

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Acknowledgements

The authors acknowledge the financial support of the project of the Economic Development and Innovation Operative Program of Hungary, GINOP-2.3.2-15-2016-00053: Development of liquid fuels having high hydrogen content in the molecule (contribution to sustainable mobility). The Project is supported by the European Union.

OP-III-5

CATALYTIC APPROACHES FOR THE PROCESSING OF PYROLYSIS BIOMASS PRODUCTS

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The technologies of fast pyrolysis are applied to pyrofuel production, however taking into account its low operating ability (high oxygen content and corrosion activity) it is necessary to search for the new technological solutions [1].

To generate electrical energy from plant-based biomass waste the fast pyrolysis technologies focused on the increase of the conversion of the initial raw material to the combustible gases with high heat value and low tar content are more preferable [2].

Thermocatalytic refining of gaseous products of pyrolysis is one of the technological methods focused on the decrease of the content of high-boiling fractions and tars. The gaseous products of the pyrolysis flow through the catalyst layer that result in the thermal destruction of high-boiling components and tars. The significant amount of gaseous hydrocarbons form in the thermocatalytic destruction of pyrolysis gases tars. They increase the “working” combustion heat of the pyrolysis gaseous products.

Catalytic pyrolysis causes a significant interest all over the world because the use of catalysts promotes the growth of the effectiveness of organic compounds processing [3, 4]. The use of catalysts in the organic source conversion process allows increasing of liquid and gaseous products yield as well as increasing of concentration of aromatic compounds and branched hydrocarbons in liquid pyrolysis fraction. Products obtained by catalytic pyrolysis have much more narrow range of the molecular mass distribution in comparison with non-catalytic process. So these products carry the higher quality and can be used as the transportation fuels, it is an important benefit of catalysts application in the waste pyrolysis process [5, 6].

The biomass fast pyrolysis process was carried out under inert atmosphere (nitrogen). The feedstock mass loaded into the reactor was 500 g. The total time of the experiment was 30 min. To estimate the rate of thermodestruction of initial source in the presence of the catalysts the rate of gaseous products evolution was controlled during the experiment.

The gaseous products analysis was performed by the gas chromatography method. The analysis of the fast pyrolysis gaseous products consisted of C_1-C_4 hydrocarbon, carbon oxides and hydrogen content definition, as well as the express analysis of the lower specific heat value. The chromatographic analysis of the gaseous products was performed on the base of chromatograph “Kristallux” 4000M and modified chromatograph “Gasochrom 2000”.

The use of metal-containing alumosilicate catalyst in the pyrolysis gas refining from the tars results in the change of the gas volume and heat value. The use of the studied zeolite catalysts containing the iron subgroup metals leads to the change in the concentration of hydrogen, C_1-C_4 hydrocarbons and carbon oxides.

The concentration of metal on the surface of the alumosilicate catalyst strongly affects the catalyst activity in the thermodestruction process of a pyrolysis gas tars. The gaseous product composition in dependence to the type and concentration of the metal on the catalyst surface. In comparison with a non-catalytic process the volume concentration of C_1-C_4 hydrocarbons increases by 1.39; 1.66 and 1.52 times using Fe-containing, Co-containing and Ni-containing alumosilicate catalysts respectively.

The use of the catalysts also results in the increase in hydrogen concentration; moreover the growth of hydrogen concentration in a gaseous product increases from Fe to Ni. The increase in alumosilicate catalyst metal content also leads to the increase in hydrogen concentration that is caused by the dehydration reaction of pyrolysis organic products in the presence of iron subgroup metals. The growth of hydrogen concentration in a pyrolysis gas is accomponied by the increase in coke-formation on the catalyst surface, so the use of the catalysts with higher metal content is economically unfavorable. The considerable effect of the studied catalysts on the pyrolysis gas composition can be explained both by the catalyst high activity in the thermodestruction process and thermal decomposition of high-boiling fractions of pyrolysis liquid products. According to the data on the gaseous product composition the optimal Co content in the zeolite catalyst is 2 % (wt.). Such metal content in the catalyst allows increasing C_1-C_4 hydrocarbons concentration and removing the tars from the combustible gas of the fast pyrolysis of the studied types of biomass.

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Acknowledgement

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DEHYDRATION OF CARBOHYDRATES INTO FURANIC PRODUCTS BY PROMOTED SULPHATED METAL OXIDES CATALYSTS

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1. Scope: Lignocellulose biomass, a plentiful source of carbohydrates, such as xylose (XYL) and glucose (GLU), which can be catalytically converted to high value chemicals and biofuels. XYL can be converted to furfural (FUR), whilst, GLU can be converted to 5-hydroxymethylfurfural (HMF), both promising key green platform chemicals providing chemical building blocks for the pharmaceutical, agricultural, and petrochemical industries. Novel and efficient solid catalysts are required to replace corrosive homogeneous catalysts such as H_2SO_4 and HCl, currently used in the chemolytic conversion of carbohydrates. Bulk and modified metal oxides are opportune catalysts due to their high concentration of actives sites, compositional variability and coexistence of Brønsted-Lewis acid sites. This work reported here investigates diverse bulk and bifunctional oxides, composed of SnO_2, TiO_2 or ZrO_2. They were prepared following the method described by Matsuhashi et al. [1]; however, various synthesis modifications were included (molar ratios of active metals, H_2SO_4 treatment and calcination temperature). Their physico-chemical properties were evaluated using XRD, FTIR, elemental analysis, XPS and TPD. The catalytic activity of the synthesized catalysts was investigated through the conversion of XYL (0.3 M) and GLU (0.2 M) to FUR and HMF, respectively. Aqueous phase reactions were carried out under mild temperatures (120-170 °C) and autogenous pressure (40-90 psi).

2. Results and discussion: The properties and catalytic activity of bulk sulphated tin oxide (Sn_{500}) and sulphated titanium oxide (Ti_{500}) were compared to the bi-functional catalysts $3SnTi_{500}$, $3ZrTi_{500}$, and $3ZrSn_{500}$. The latter catalysts are described as *nBMt*, where *B* and *M* represent the secondary and the main compound, respectively, *n* represents the composition of the secondary compound and *t* the calcination temperature, e.g. $3SnTi_{500}$ refers to 3:7 ratio of Sn:Ti, calcined at 500 °C. The XRD diffraction peaks of $3SnTi_{500}$ were broader than those for $3ZrTi_{500}$ due to the significant uptake of Sn on the supported phase (see **Fig. 1**). Distinct interactions between the phases were observed affecting the crystallite size of the catalysts. The use of Zr in the tin oxide catalyst increased the crystallite size of the material; however, Sn and Zr had the opposite effect on the Ti-based catalysts. Additionally, increasing the calcination temperature had a significant effect on crystallite growth due to the corresponding rates of loss of H_2O and SO_3 achieved.

The Sn_{500} and $3SnTi_{500}$ gave the highest FUR yields at 120 °C, Y_{FUR} = 13 and 20 mol %, respectively, as seen in **Fig. 2**. Despite the increase in the crystallite size, the addition of Zr to the tin oxide catalyst in $3ZrSn_{500}$ did not improve the FUR formation due to the promotion of side products. The $3SnTi_{500}$ catalyst had a higher catalytic activity than their Ti-based counterparts. This indicated that acidity and surface activity may play a greater role than surface area as correlated by the crystallite size. Additionally, variations of the synthesis conditions showed that lower calcination temperatures gave higher FUR selectivities due to the greater capacity of these catalysts to retain sulphur on its active surface (**Fig. 3**). At 120 °C, the $7STi_{350}$ catalyst showed the highest FUR selectivity (S_{FUR} = 33 mol %, Y_{FUR} = 20 mol %) in a shorter reaction time (4 h) than the other Ti-based catalysts. Furthermore, similar trends were observed for the GLU conversion. Among the bulk and bi-functional catalytic systems, the $3SnTi_{500}$ catalyst gave the highest HMF yield (Y_{HMF} = 9 mol %) at 120 °C. However, a major distinction regarding the chemo-selectivity to HMF was seen for the various SO_4^{2-}/SnO_2-TiO_2 catalysts with different composition ratio and calcination temperatures. The $7STi_{350}$ catalyst showed the highest selectivity (S_{HMF} = 24 mol %, Y_{HMF} = 11 mol %) after 6 h at 120 °C.

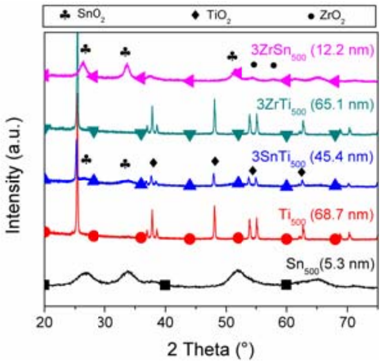

Fig. 1. XRD patterns and crystallite size of catalysts Sn_{500}, Ti_{500}, $3SnTi_{500}$, $3ZrTi_{500}$, $3ZrSn_{500}$. Crystallite size indicated in brackets

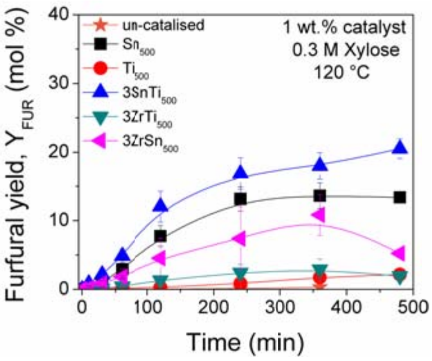

Fig. 2. Comparison bulk and bi-functional catalysts.

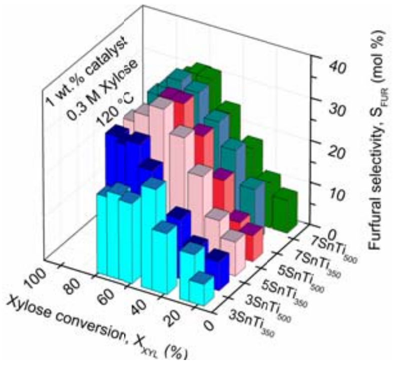

Fig. 3. Effect of ratio composition and calcination temperature

3. Conclusions: For the first time, the SnO_2-TiO_2 catalysts were used in the dehydration of carbohydrates, which presented better physicochemical properties to attain higher catalytic activities. This study contributed to enhancing the study of the state-of-art of the green energy technologies.

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CATALYTIC FRACTIONATION OF LIGNOCELLULOSE USING NON-NOBLE METAL CATALYSTS

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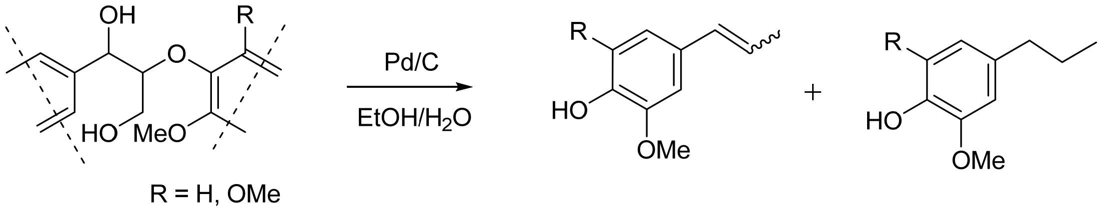
Lignin is the most abundant aromatic polymer on earth, and therefore an attractive feedstock for renewable chemicals. The lignin produced by traditional pulping methods is a challenging substrate for selective transformations due to low purity and condensed chemical structure, and so far most of lignin is burned in pulp mills. Combining biomass delignification with catalytic conversion of lignin into aromatic monomers provides a promising approach for lignin valorization [1]. The fractionation targets especially the 'β-O-4' linkages, which is the most common bonding motif in lignin. Importantly, converting lignin fragments directly into less reactive products prevents repolymerization, and high monomer yields can be obtained. Fractionation can be performed under oxidative, reductive or inert conditions and respectively, aryl aldehydes, alcohols or alkyls are reported as main products from lignin.

Several heterogeneous catalysts (e.g. supported Ni, Ru, Rh, Pt, Pd) have been reported for hydrogenolysis of lignin using both pressurized hydrogen and transfer hydrogenolysis [2]. Recently, fractionation of lignocellulose without external hydrogen source was accomplished using Pd/C (Scheme 1) [3].



Scheme 1. Main products of fractionation of biomass lignin using Pd/C [3]

In this work, we present catalytic biomass fractionation using non-noble metals (Ni, Co, Fe) supported on nitrogen-doped carbon supports. These catalysts have recently shown fascinating activities in a range of transformations, e.g. hydrogenations and oxidations under mild conditions [4]. The catalysts are prepared using simple procedures from common and inexpensive metals.

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Developing robust and recyclable heterogeneous catalysts for lignin valorization is a crucial step towards efficient conversion of biomass into valuable chemicals.

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RECENT TRENDS IN BRAZILIAN BIODIESEL PRODUCTION

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Despite of tremendous effort to develop second generation biofuels, most of the expected new technologies has failed from a technical point of view due to small yields, extensive maintanance or because economic drawnbacks like high capital expenses (CAPEX) or significant amount of co-products to be developed in the market [1-3]. Meanwhile, first generation biofuel programs like ethanol and biodiesel keep growing in several countries, mainly outside Europe. Brazil, for instance, is the second largest biodiesel producer in the world and its production will probably to double in 3 or 4 years with a strong mandatory program officially achieving B10 in 2018 with a B20 projection in the next decade [4-5]. Part of this success is ascribed to a similar final price as compared to fossil diesel even without subsids. Learning curve of biodiesel production is a clear fact when you evaluate the last ten years when the first biodiesel plants started to produce in Brazil. Nowadays, not few ones have more than one million liters/day capacity but scale up has not been the only one factor to explain how this biofuel became feasible in some countries. In addition to available raw materials, engineering has played a very important role in this field. Sodium methylate transesterification catalyst consumption now is smaller than in the first plants, even with the higher yields (more than 99 %) which are regularly obtained in the current factories. Antioxidant concentration has also decreased despite higher oxidative stability values have been required in the new biodiesel standarts. Probably, one of the most important advances has been the development of esterification reactors in order to use lower prices raw materials with higher acid numbers. From the original batch reactors with very corrosive catalysts like sulphuric acid, new plants are using continuous esterification reactors working with solid catalysts or even with higher pressure and no catalyst. Figure 1 describes the concept of reactive distillation system which has been already applied in current biodiesel industries.

OP-III-8

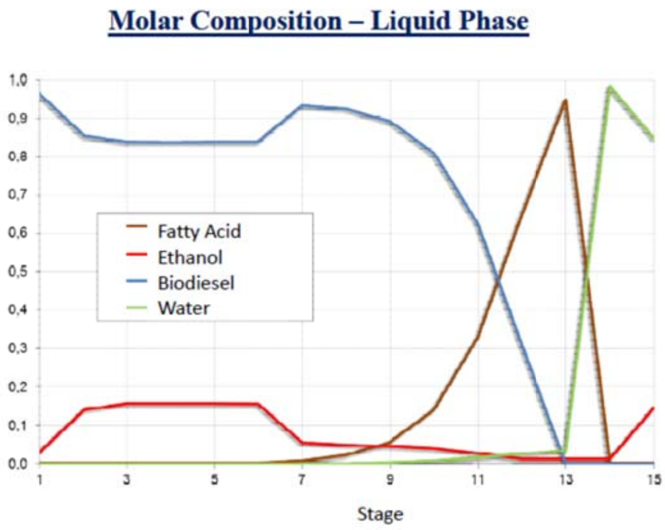

Figure 1. Reactive Distillation Column: Molar Composition in the Liquid Phase for Esterification of Fatty Acids

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HYDROTHERMAL STEARIC ACID DECARBOXYLATION OVER (1 % wt. Pd)-SUPPORTED (C, SiO_2, Al_2O_3 or Nb_2O_5) CATALYSTS

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Introduction

A one-pot catalytic hydrolysis-decarboxylation reaction is one of the potential route to produce green diesel or value-added chemicals such as α-olefins by using natural fats and vegetable oil-based feedstocks. Nickel and/or palladium catalysts are good candidates to carry out both reactions sequentially in the same conditions. However, the decarboxylation of the fatty acids, which are in the feeding or produced in the hydrolysis reaction, in an aqueous reaction media is less effective and described in the literature than the organic one. Then, the main goal of this work is to investigate the stearic acid (SA) hydrothermal decarboxylation by using palladium supported on different supports (C, Al_2O_3, SiO_2, Nb_2O_5).

Experimental

The catalysts (1 wt. % Pd) were prepared by incipient wetness impregnation of an aqueous $[Pd(NH_3)_4](NO_3)_2$ solution, dried at 120 °C and calcined at 300 °C (except on C). They were characterized by H_2-TPD, CO-chemisorption, and other techniques. The reactions were performed in a 500 mL-stirrer batch reactor at 25 bar and 250 °C during 3 h by using SA/H_2O/catalyst mass ratio of 1/100/5.

Results and Discussion

Heptadecane was the unique organic molecule observed in the GC-FID analysis after reaction, indicating a selective decarboxylation reaction. Figure 1 reveals that the final decarboxylation conversion was reached at less than 1.5 h with all catalyst. It also exhibits the maximum specific rates after 1.5 h and the turnover frequency (TOF) as well. The results can be explained by the metallic sites density and strength.

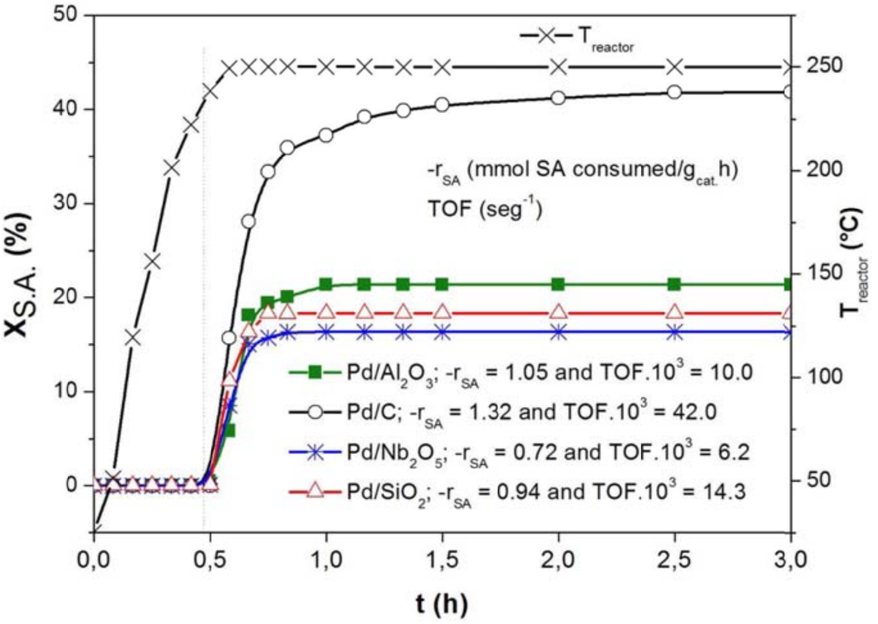

Figure 1. SA decarboxylation catalytic activities

Conclusions

Pd/C catalyst exhibits the highest conversion of stearic acid and heptadecane yield as well. Then, this catalyst can be used in a final step (catalytic bed) for a sequential hydrolysis-decarboxylation reaction or as base for new multifunctional catalyst, which can performs all the sequential reactions.

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OP-III-10

COMBUSTION SYNTHESIZED COBALT CATALYSTS FOR FISCHER TROPSCH SYNTHESIS

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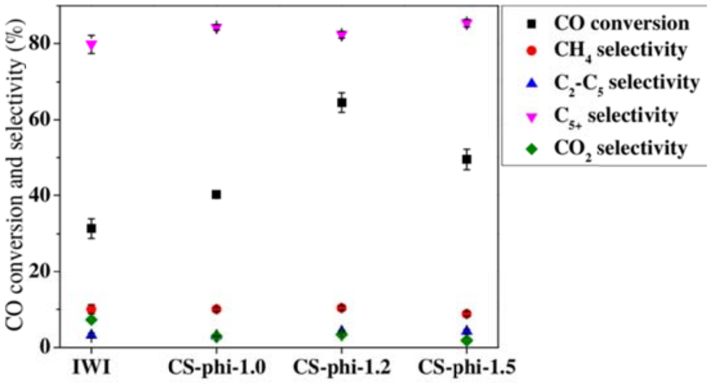
This work is concerned with the conversion of syngas to liquid hydrocarbons via the Fischer Tropsch reaction using cobalt catalysts. The γ-Al_2O_3 supported cobalt catalysts are synthesized by incipient wetness impregnation (IWI) method and the combustion synthesis (CS) route. CS catalysts were synthesized using hexamethylenetertramine as the fuel[1]. In particular, a novel method of catalyst synthesis was designed to reduce the metal-support interaction and increase the fraction of reducible cobalt oxides and the metal dispersion – that were observed and analysed using the X-ray photoelectron spectroscopy and H_2 chemisorption. Alternatively, the role of combustion stoichiometry (equivalence ratio, φ) were investigated for its effect of the catalyst properties, viz., crystallite size, degree of reduction, Co dispersion and the metal support interaction. The Al_2O_3 supported CS catalysts resulted in an increased FT activity, as the CO conversion increased from 32 % for IWI catalysts to 41 % for CS catalysts. Similarly, enhanced CO conversion rates were observed for CS catalysts synthesized with φ=1.2 and 1.5, with a highest CO conversion of 61 % for CS (φ = 1.2). Strikingly, the FT product spectrum reported a maximum weight fraction of wax hydrocarbons (C_{24+}), allowing for higher degree of surface polymerization for CS catalysts. Figure below shows the CO conversion and selectivity for the synthesized catalysts. An assessment is made on the conversion of biomass to liquid fuel via oxy-steam gasification and Fischer Tropsch reaction.



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Pd-CONTAINING CATALYSTS IN FATTY ACIDS CONVERSION

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Nowadays the biomass conversion is of the great interest. One of the ways to process biomass is the biofuel production. Biogas, bioethanol, and biodiesel are widely used types of biofuel [1]. Biodiesel is the one of the perspective type of biofuel. Typically biodiesel is obtained from oils and fats through methanolysis with use acid or based catalysts. Biodiesel made by this method has such drawback as poor stability due to the oxygen presence. In addition, biodiesel production requires the use of raw with certain quality. For example, waste oil and frying fat are not desirable due to the high concentration of free fatty acids.

The most promising way for biodiesel synthesis is the biomass hydrofining. Hydrofining includes following processes – hydrodeoxygenation, hydrocracking, hydrogenation – to produce 2nd generation biodiesel in form of linear saturated hydrocarbons with carbon number of 15-22 [2].

2nd generation of biodiesel is mixing easily with mineral diesel. Moreover it has higher cetane number, higher energy content, excellent combustion quality, good low-temperature properties, and superior thermal stability, storage stability, and materials compatibility in comparison with both petrol diesel and biodiesel [3].

In this investigation the hydrotreatment of fatty acids was carried out. The stearic acid (99 %, KhimMedService, Russia) was used as the model substrate. n-Dodecane (99.9 %, Sigma-Aldrich) was used as a solvent. Palladium supported on hypercrosslinked polystyrene (HPS) of MN270 type (Purolite LTD, UK) was used as a catalyst. The metal loading was varied from 1 up to 5 % (wt.). The process was conducted in stainless steel batch reactor PARR-4307 (USA). The following reaction conditions was varied: hydrogen pressure 0.2-2.5 MPa, temperature 100-260 °C, concentration of stearic acid 0.05-0.2 M. Liquid samples were taken every hour during the process and analyzed using GC-MS.

The catalyst structure was studied using the following physico-chemical methods: low-temperature nitrogen physisorbtion, transmission electron mycroscopy, X-Ray photoelectron spectroscopy, IR-spectroscopy, thermogravimetric analysis.

A comparison of catalytic activity was made by TOF value (Figure 1). It was found that HPS-based catalyst with Pd loading 1 (wt.) % seems to have the highest catalytic activity and selectivity regarding to the target products in both investigated reactions.

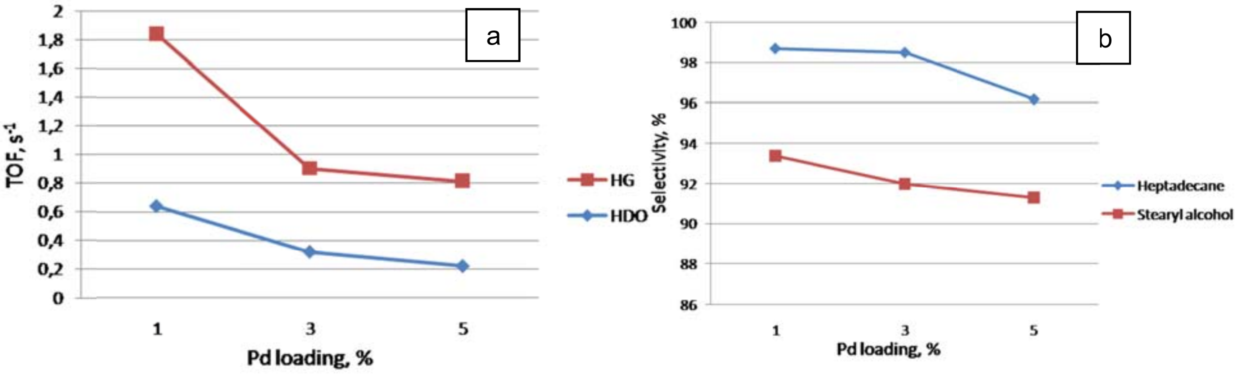

Figure 1. TOF value (a) and selectivity regarding to target product (b) for HPS-based catalysts in hydrodeoxygenation (blue lines) and hydrogenation (red lines) of stearic acid

It is noteworthy that the selected catalyst (1 %-Pd/-HPS-MN-270) remains its activity and selectivity regarding to the target product at the multiple usage (up to 20 times) in both reactions. Moreover for selected catalyst there were chosen optimal process conditions for hydrodeoxygenation as well for hydrogenation reaction. Basing on the kinetic experiments the apparent activation energy was calculated and was 85±5 kJ/mol for hydrodeoxygenation process and 60±5 kJ/mol for hydrogenation reaction.

During the study it was found, that the most effective catalytic system for all investigated processes was the catalyst 1 % Pd/HPS-MN-270, which has high surface area (1300 m^2/g) and average pore size 4-6 nm. This catalyst allows achieving the high products yield in hydrodeoxygenation and deoxygenation processes (selectivity regarding n-heptadecane was 99 % at 100 % substrate conversion) as well as in hydrogenation reaction (selectivity regarding stearyl alcohol was 93.8 % at 100 % substrate conversion) of stearic acid chosen as model substrate.

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OP-III-12

PRODUCTION OF JET FUEL CONTAINING MOLECULES OF HIGH HYDROGEN CONTENT

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The plastic production of the World and the European Union was increased to 322 and 58 million tonnes in the year of 2015 [1]. Due to the excellent properties of plastics their application has been increased. In 2014, 25.8 million tonnes of plastic waste was generated in the European Union, of which 30.8 % was sent to landfill. Packaging industry (30.9 %) as one of main waste producers generated plastic waste with the following average composition PP (19.1 %), PE (29.4 %), PVC (10.1 %), PS (6.9 %) and PET (7.1 %) [1]. Despite landfilling of waste plastic was reduced steadily, the present scenario has been still inadequate. Plastics are unable to degrade in a reasonable time, and they cause harmful effect to the environment. Among the methods of waste management the chemical recycling (e.g. cracking) is the most promising option. In the literature catalytic and thermal cracking of PP, PE and PS were examined most widely [2-3], but several research groups carried out cracking by using other types of wastes, too [4-5]. The cracking products contain free radicals, causing polymerization and resin formation, therefore their oxidation stability is not adequate, additionally the freezing point of PE cracking products rich in α-alkene and linear alkane compounds can be higher than -47 °C. Nonetheless, limited information is only available about experiments made by the kerosene boiling point range part of cracking products [6-7]. Aim of the reported experiments mainly was to study the variation of yield and composition of hydrogenated products in a function of the process parameters, and properties regarding to JET fuels (e.g. freezing point, smoke point) were not measured. Additionally, the reported measurements generally carried out in batch reactor. The aim of our experimental work was to study the quality improvement of kerosene fractions produced by mixing the appropriate fraction of waste PE cracking in different ratios (10 %, 20 %, 30 %) with high sulphur straight run kerosene, and effects of process parameters (T = 200-300 °C, P = 40 bar, LHSV = 1.0-3.0 h^{-1}, H/C ratio = 400 Nm^3/m^3) on the product yields and properties were also investigated. At favourable process parameters practically olefin and sulphur free (Figure 1.) products having high energy and hydrogen content were produced, additionally they provide excellent burning properties and meet the requirements of the JET fuel standard, consequently they can be used directly in jet engines and fuel supply infrastructure being used currently.

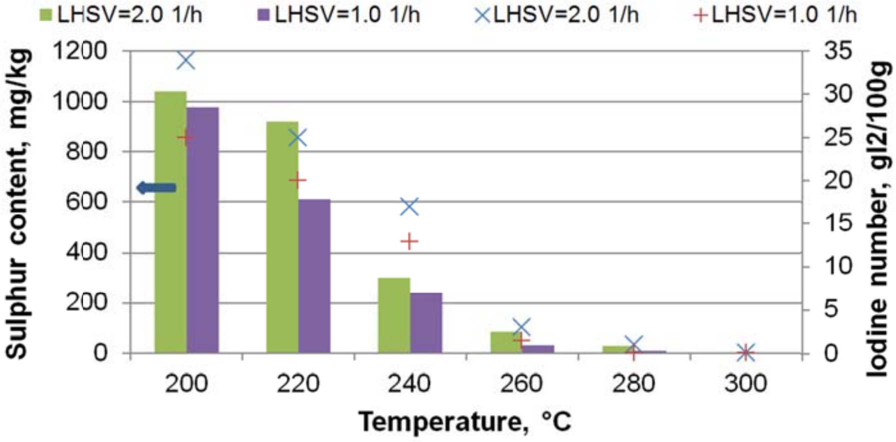

Figure 1. The sulphur and olefin content of the liquid products in the function of the temperature (P = 40 bar, cracking product content: 30 %)

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OP-III-13

QUALITY IMPROVEMENT OF WASTE POLYOLEFIN ORIGINATED GAS OIL FRACTIONS ON TRANSITION METAL/SUPPORT CATALYST

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The amount of bio-components used in fuels is continuously growing in Europe. The “Clean Energy For All Europeans” package of the European Commission (2016) establishes an EU-level obligation for fuel suppliers to provide a certain share (6.5 % in 2030) of renewable fuels having low greenhouse gas emission and the decreasing maximum share of biofuels and bioliquids produced from food or feed crops starting from 7 e% (2021) to 3.8 e% (2030). Therefore it is important to produce new, e.g. waste-based, low carbon fuel components.

The amount of waste in the EU is circa 1828 kg per capita. The amount of plastic waste is 34 kg/capita, from which 40 % is disposed in landfills [1]. From the plastic waste processing technologies the chemical recycling can be used to produce hydrocarbons, which is currently takes place in case of 1 % of the plastic wastes [2]. The obtained highly olefinic hydrocarbon mixture cannot be used as engine fuel, quality improvement is needed [3]. In this field there are only a few research data available.

Therefore the aim of our work was to produce high quality diesel fuel blending components. In this work the quality improvement of gas oil blends produced from waste polyolefin thermal cracking (5, 10, 20 and 30 %) and different quality, unrefined crude oil based gas oil fractions with high sulphur- and aromatic contents was studied. During the experiments the hydrogenation of the instable olefins and the influence of olefins to the desulphurisation and aromatic saturation reactions were investigated. The effect of the process parameters (temperature: 300-360 °C, pressure: 50 bar, liquid hourly space velocity: 1.0-3.0 h^{-1}, H_2/hydrocarbon ratio: 450 Nm^3/m^3) in the presence of Ni(2.3 %)Mo(11.0 %)P(2.3 %)/Al_2O_3 catalyst on the quality and quantity of the liquid products was studied.

The highly olefinic gas oil fraction was mixed with different quality gas oils (LGO – CFPP: -26 °C, sulphur content: 5500 mg/kg, nitrogen content: 4 mg/kg; HGO – CFPP: 0 °C, sulphur content: 6700 mg/kg, nitrogen content: 228 mg/kg) in two different experiments. The olefin content of the products from mixtures with LGO and HGO was almost the same at the same process parameters. At 300 °C and above the olefin content of each product was below 1.0 %. As shown in Table 1. the sulphur content of the products obtained from LGO mixtures was significantly lower, each product obtained at 340 °C satisfied the 10 mg/kg maximum limit prescribed in the EN 590:2013 standard. In case of HGO feedstocks only the products obtained at 1.0 h^{-1} LHSV had lower sulphur content than 10 mg/kg. The sulphur content was lower with the increase of residence time.

Table 1. The sulphur content of the products obtained from the 20 % PPGO containing feedstock (P= 50 bar)

Temperature, °C	LHSV, h^{-1}	20 % PPGO + 80 % LGO	20 % PPGO + 80 % HGO
		product sulphur content, mg/kg	
300	1.0	8	246
	3.0	97	351
320	1.0	3	85
	3.0	11	232
340	1.0	2	4
	3.0	7	114
360	1.0	1	4
	3.0	4	41

It was found that the blending of PPGO had a beneficial effect on the products performance properties. On the investigated catalyst suitable parameter combinations are determined to each raw material combinations for the production of diesel gas oil blending component with excellent properties.

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OP-III-14

GC-TCD FOR THE MEASUREMENT OF COMPONENT BY-PRODUCT OF CATALYTIC HYDRODEOXYGENATION OF BIO-OIL: TOWARD OBTAINING REALIABLE ANALYTICAL DATA

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In this study, the hydrodeoxygenation (HDO) of bio-oil by involving hydrogen and Ru/C-based catalysts was experimentally conducted and some compounds in the gasesous by-product were found. The compounds were identified as H_2, CO_2, CH_4, and CO by using gas chromatographic equipped with thermal conductivity detector (GC-TCD) method. From analytical chemistry perspective, quantitative measurement is reasonably essential by taking into account an accurate measurement process for providing reliable measured data. The measured data is commonly used as the basis for decision making in many aspect of chemical process. In this regards, the GC-TCD for the measurement of HDO gasesous product was developed and validated. The validation parameters include selectivity, precision (repeatability and reproducibility), accuracy, linearity, limit of detection (LoD), limit of quantitation (LoQ), and robustness. It was found that the developed method is able to separate the target components (H_2, CO_2, CH_4 and CO) from their mixtures without any special sample treatment and no interference from other possible components in the HDO gaseous were observed (Figure 1b). In addition, under the validation criteria, the method was found to be selective, precise, accurate, and robust. Application of the developed and validated GC-TCD method for the measurement of components by-product of HDO of bio-oil showed an outstanding performance with relative standard deviation (RSD) less than 1.0 % for all target components. In conlusion, conducting validation process of any analytical method is highly recommended before it is used for measuring a real sample and it is a trustworthy way of obtaining reliable analytical data. The method validation process presented in this study can be easily and conveniently adopt for routine analysis with regard to the measurement of compounds in the gaseous peroducts of any expremintel HDO of bio-oil

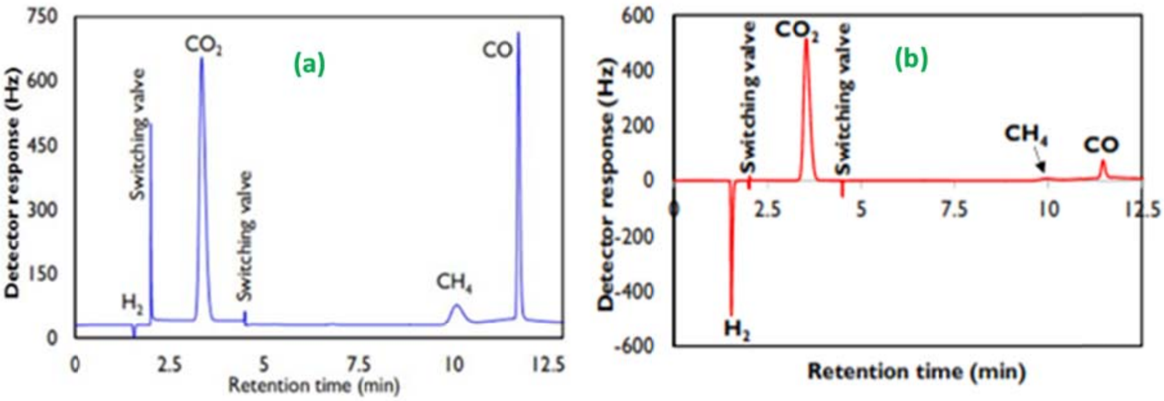

Figure 1: Representative GC-TCD chromatogram of (a) the the standard gas mixture, and (b) the HDO gaseous sample obtained using Ru/C at optimized conditions.

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STABLE CATALYST – THE KEY TO 2nd GENERATION BIOFUELS

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In recent decades the interest in biofuels has been shifted from fuels derived from edible oil and sugars towards the production of 2nd generation biofuels from lignocellulosic bio-feeds. A promising first step herein is the liquefaction of lignocelluloses by fast pyrolysis [1]. This process yields pyrolysis liquids (PO or bio-oil), possibly to be used as a co-feed in conventional fluid catalytic cracking (FCC). However, the direct integration of PO into the existing refinery infrastructure is not the best option, due to high polarity, viscosity, and the low thermal stability of bio-oil.

To optimize this value chain, the polarity of PO is to be changed mainly to lower its coking tendency, and preferably to make it miscible with vacuum gasoil (VGO). An effective instrument towards achievement of this goal is a two-stage hydrotreatment of bio-oil, including *stabilization* at 150-250 °C (1st stage) followed by *deoxygenation* at elevated temperatures 350-400 °C (2nd stage) and high H_2 pressures of 10-20 MPa [2].

One of the most important challenges is to develop catalysts which would possess sufficiently high activity, but importantly a high stability in hydroprocessing of aggressive and unstable pyrolysis oils. Recent studies have shown promises for sol-gel catalysts with high Ni loading (about 50 wt. %), denoted the Picula family of catalysts [3-5]. It was shown that modification by P/Mo-containing agents via wet impregnation significantly improved mechanical strength and resistance to corrosion of catalysts [6].

In the present study a further modification of Picula catalyst NiCu-SiO_2 has been proposed enabling intimate interaction between components, by the addition of Mo- and P-containing agents *prior* to the sol-gel stage. A stepwise approach to study these catalysts allowed us to find optimized composition in terms of activity and stability.

First the effect of Mo on Picula performance was investigated in the hydrotreatment of guaiacol (GUA), as a model for lignitic species in PO (batch reactor, 320 °C, constant H_2 pressure of 9 MPa). The selectivity for deoxygenation was observed to increase with Mo content, attributed to changes in active component nature. According to TPR, XRD, XPS and HRTEM data, the observed effects were associated with the formation of NiMo(Cu) solid solutions and coordinately unsaturated surface Mo^{x+} sites.

In a second stage, two Mo-containing Picula catalysts (denoted as Picula-Mo-1 and Picula-Mo-2) were used for ‘stabilizing’ the pure bio-oil (continuous flow setup, 210-215 °C, 7.5 MPa), and showed better characteristics of process and product compared to an unmodified $NiCu-SiO_2$ system. The presence of Mo significantly suppressed agglomeration of active metallic Ni particles likely due to their hindered mobility in the presence of hardly reducible molybdenum oxides and the formation of Ni-Mo solid solutions.

Finally, phosphoric acid was used to modify the most promising Picula-Mo-1 catalyst, again *prior* to the sol-gel stage. A series of P-modified (1.5, 3 and 5 wt. %) Picula-Mo-1 was studied in PO stabilization in a batch reactor at 230 °C. Despite the lower hydrogenation activity of P-containing Picula compared with the pure catalyst, possibly related to lower active component surface, their thermal stability was increased significantly as evidenced by XRD and HRTEM. Along with outstanding stability to agglomeration, the system denoted as Picula-Mo-1-5P showed a remarkable resistance in model 1M acetic acid not previously observed, and accounted for by the formation of very stable Ni phosphides. Thus, the advanced approach proposed in the study allowed the development of highly stable catalyst which is the key for efficient PO hydrotreatment into products suitable for co-FCC.

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PREDICTING ZSM-5 PROPERTIES AND ACTIVITY IN CONVERSION OF ALCOHOLS TO FUEL RANGE HYDROCARBONS; AN ARTIFICIAL INTELLIGENCE APPROACH

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Introduction

Fermentation broth obtainable from organic materials is a potential source of ethanol [1]. The vision of using ethanol from fermentation as a universal feedstock for production of chemicals and fuels is surely one of the promising routes towards sustainable production. Bioethanol could be dehydrated to yield ethylene which could undergo a number of reactions that will produce priceless chemicals. The product distribution of ethanol conversion is majorly determined by the quality of ethanol, operating conditions as well as the catalyst employed in the process. While zeolites have been known to show good activity in ethanol conversion to fuel range hydrocarbons, other catalysts like cerium oxide are known to favour the production of hydrogen. The Fischer Tropsch process uses iron and cobalt catalysts for the production of different hydrocarbons [2]. The activity of these active components could also play a vital role in the transformation of ethanol to fuels and petrochemicals. This work investigates different techniques of promoting synthesized ZSM-5 zeolites with iron, cobalt and nickel as well as the efficiency of techniques with respect to catalyst activity and selectivity. The work further utilizes design expert and artificial neural network in developing models that predict catalysts activities and selectivity.

Materials and Methods

A series of ZSM-5 catalysts were synthesized hydrothermally using aluminum salts and water glass as sources of alumina and silica respectively. The reagent composition was determined by the target ZSM-5 SiO_2/Al_2O_3. The pH of the batch mixture was kept below 10.8. The batches were further aged at different times (0-48 hrs.) and crystallization was done at different temperatures and times not exceeding 200 °C and 96 hours respectively. The produced crystals were processed by filtration, calcination and protonation to synthesize the desired protonated form of the catalyst. A commercial zsm-5 was also purchased from Zeolyst for comparative studies with the in house catalyst.

Nitrates of cobalt and iron were used for promotion at different loadings (5 %, 10 % and 15 %). Mechanical mixing, co-precipitation and incipient wetness impregnation were applied as promoting techniques to enhance catalyst performance. The synthesized catalysts were characterized using XRD, BET, XRF and SEM.

The catalyst activity was tested using a fixed bed reactor at different space velocities and temperatures in the range of 200-450 °C. The feed used include ethanol and water mixtures of various composition, isopropanol and butanol. Other alcohols were investigated so as to have a better understanding of the most probable reaction path during ethanol conversion. Design expert and Artificial Neural networks were used as a guide in developing models for predicting catalyst properties

Results and Discussion

Powder XRD patterns of the catalyst synthesized confirmed the presence of 2 theta values for the target ZSM-5 catalysts. Figure 1 shows the diffractogram of the synthesized zsm-5 catalyst. The presence of the zsm-5 characteristic peaks at 2 theta = 7-9° and 23-25° further confirm the successful synthesis of zsm-5. All the synthesized material had relative crystallinities of not less than 90 % when compared to the commercial zsm-5 catalyst. The BET surface area and particle sizes are all seen to be a function of aging. The SEM analyses further confirmed that the zeolites formed were crystalline and had different morphologies depending on the technique used in incorporating the promoter and synthesis conditions. Figure 2 shows the micrograph of un-promoted zsm-5 with average particle size of 0.2 μm. The incorporation of metals altered both the particle morphology as well as size.

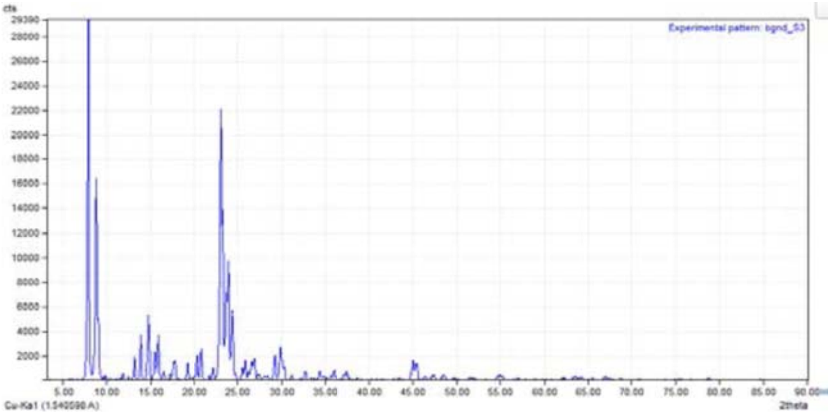

Figure 1. Diffractogram of synthesized zsm-5

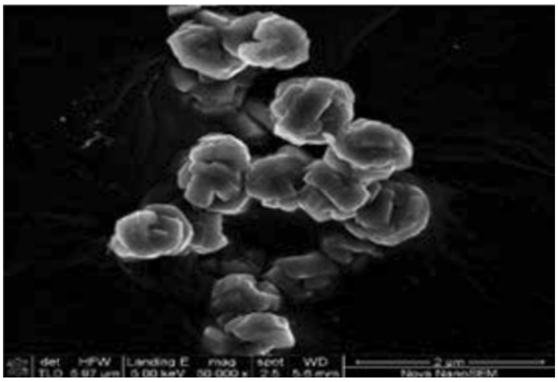

Figure 2. Micrograph of synthesized ZSM-5

All the catalysts showed 100 % activity for ethanol and isopropanol conversion with liquid hydrocarbons forming a significant amount of the products. Loading of 5 % iron oxide on the commercial catalyst by incipient wetness impregnation showed selectivity to gasoline range hydrocarbons of 72 % in the liquid products whereas the in house catalyst showed a better selectivity of 98 % during ethanol conversion. Co crystallization of both commercial and in house ZSM-5 showed different selectivity when compared to the unpromoted zsm-5. However, 5 % loading of nickel showed the highest selectivity towards gasoline range hydrocarbons (99 %) when ethanol was used as a feedstock. Interestingly, the prediction factors from using artificial intelligence was greater than 0.8 for both catalyst properties and selectivity to certain hydrocarbons.

Significance

For the first time in open literature, artificial intelligence has been used to predict zeolite properties as well as selectivity in ethanol conversion. This will serve as a basis for application in other areas like water treatment where certain zeolite porosities are required.

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ORAL PRESENTATIONS

Section IV. BIO-PHOTO-/ELECTRO-CATALYTIC CONVERSION OF RENEWABLES

Bio-catalysis for chemicals production
Photo-catalytic for environmental protection
Electro-catalytic conversion of renewables

VALORIZATION OF LIGNIN RESIDUES - BIOCATALYTIC OXY-POLYMERIZATION OF MONO-/OLIGO-LIGNOLS LEADING TO ARTIFICIAL LIGNIN STRUCTURES

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Lignin, the second most abundant natural polymer after cellulose of terrestrial sources plays a negative role in pulp and paper industry. Huge amount of lignin is/was produced during the paper manufacturing approach (*e.g.* over 70 million tons of lignin produced annually in the world). Most of this lignin is burned (95 %) and only few percents are invested in value-added products, specially phenolic polymers.

In this context, we developed a biocatalytic system based on the oxy-polymerization of lignin waste-units (monolignols such as sinapyl alcohol SA and coniferyl alcohol CA) assisted by the enzyme (*e.g.* peroxidase enzyme) and using the oxidation reagent as enzyme cofactor (*e.g.* hydrogen peroxide H_2O_2 or tert-butyl hydroperoxide t-BHP). The process involved a radical mechanism leading to polyphenols (artificial lignin).

Controlled architecture of the prepared polymers has been done using specific type/ratio of monolignols. Additionally, well-known monomers following always the same reaction route give the opportunity for diminishing the heterogeneity of ligno-polymeric products, which is an important advantage.

Different peroxidase enzymes (e.g. unspecific peroxidase PADA-I, and versatile peroxidase 2-1B and R4) were tested exhibiting similar catalytic activity for the same monolignol (Figure 1). Oppositely, horseradish peroxidase (HRP) was not a suitable candidate for this system. As a general remark, SA was easier recognized and transformed by peroxidase compared to CA. Fast kinetic of the biocatalytic process allowed to achieve maximum conversion of the lignin fragments (around 90 % for couple of 4R and SA) in only 2 hours (Table 1). Also, large polymer structure was produced with 4R peroxidase enzyme (MW = 3188 Da and PD = 3) (Table 1).

Detailed study of the process kinetic and optimization of the experimental parameters (*e.g.* reagents concentration, temperature, buffer pH, enzyme content, etc.) have been performed. Moreover, the characteristics of the synthetic biopolymer have been investigated (*e.g.* GPC and NMR analysis) and compared to the mother-lignin source.

Table 1. Peroxidase screening for oxy-polymerization of monolignols. (Experimental conditions: 2 mg mL^{-1} lignin monomer, 0.6 % H_2O_2 and 2.582 U mL^{-1} enzyme shacked (100 rpm) at 50 °C for 2 h).

	SA				CA			
	HRP	**PaDa-I**	**2-1B**	**4R**	**HRP**	**PaDa-I**	**2-1B**	**4R**
C (%)	30.2	84.2	89.6	90.2	34.9	50.2	52.5	48.8
Mw	555	226	721	3188	2130	586	677	859
Mn	446	214	582	1115	1889	575	670	733
PD	1.244	1.056	1.239	2.859	1.128	1.019	1.01	1.172

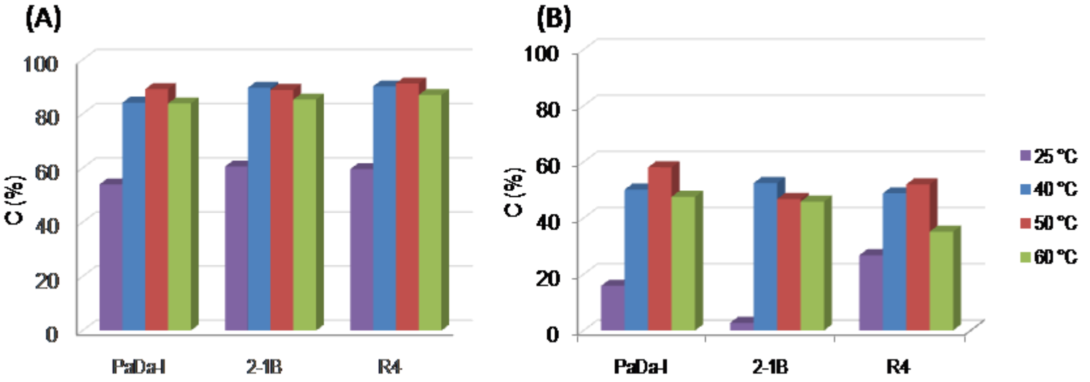

Figure 1. Polymerization of (A) SA and (B) CA lignin monomers using different peroxidase enzyme at varied temperature. (Experimental conditions: 2 mg mL^{-1} lignin monomer, 0.6 % H_2O_2 and 2.582 U mL^{-1} enzyme shacked (100 rpm) for 2 h)

The efficiency of the process related to the resulted lignin can be easily modulated based on the composition of the precursor mixture (*i.e.* content of the mixture in terms of the monolignols ratio). Therefore, a mixture of both monolignols has been used for polymerization. For co-polymerization, maximum conversion was achieved at 50 °C with H_2O_2 as oxidation reagent. However, in order to produce large lignin structures, *t*-BHP has to be used leading to a polymer with MW around 2000 Da.

Further, oligolignols from natural lignin degradation were succesefully tested in the developed system. A corelation between oligolignols structure and design/properties of the resulted artificial lignin has been found giving the opportunity to develop the requested lignin structures.

This study offers new perspective on the valorization of the lignin residues (mono-/oligo-lignols). Thus, several applications of the developed system are predicted for the future, e.g. direct deposition of the artificial lignin on the solid surface, removing the lignin fragments from the pyrolitic polysaccharides, etc).

Acknowledgments

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PHOTOCATALYTIC ACTIVITY, INFLUENCE OF THE STRUCTURE OF TiO_2 AND ITS SURFACE PROPERTIES

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The photocatalytic activity of titanium dioxide was tested in the degradation of organic substrates, mainly formic acid, phenol and aniline, in comparison to different types of titanium dioxide. The photodegradation and mineralization rate of formic acid, aniline and phenol dissolved in water were evaluated. The results have shown that the maximum value of the intermediates depends instead on the percentage of a substance already degraded, and then this value decreases (1). On the contrary, it was seen that mineralization of aniline is very low compared to the first substance (2).

The photodegradation and mineralization of formic acid show that there is no corporation with the last properties studied but it appeared an important type of degradation which can be explained. So, we added FTIR studies to complete the study about photodegradation in different types of TiO_2.

Keywords: TiO_2; photocatalytiques; phenol; aniline; formic acid.

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OP-IV-3

ELECTROCATALYTIC PRODUCTION OF HYDROGEN USING IRON SULFUR CLUSTER

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In response to the energy crisis, rising fossil fuel costs and global climate warming, this study focuses on the electrocatalytic reduction of proton into hydrogen using an iron sulfur cluster in the presence of pentafluorothiophenol. The direct reduction of pentafluorothiophenol at vitreous carbon electrode occurs at E_p -1.3 V *vs* Ag/AgCl in $[Bu_4N][BF_4]$-DMF solution. Interestingly, in the presence of $[Fe_4S_4(SPh)_4][Bu_4N]_2$, the reduction potential shifts significantly to -0.98 V *vs* Ag/AgCl. Based on gas chromatography analysis, the formation of H_2 has been confirmed with a current efficiency of *ca.* 63 % after two hours, while the chemical yield at the carbon electrode was about 46 %. On the other hand, no H_2 gas was detected without catalyst. Importantly, the increment of the concentration of acid (up to 18 equivalents) led to a positive shifting in the reduction potential until a value of 0.18 V. These results reflect the exquisite electrocatalytic efficiency of the protein-like iron sulfur cluster in Hydrogen Evolution Reaction (HER).

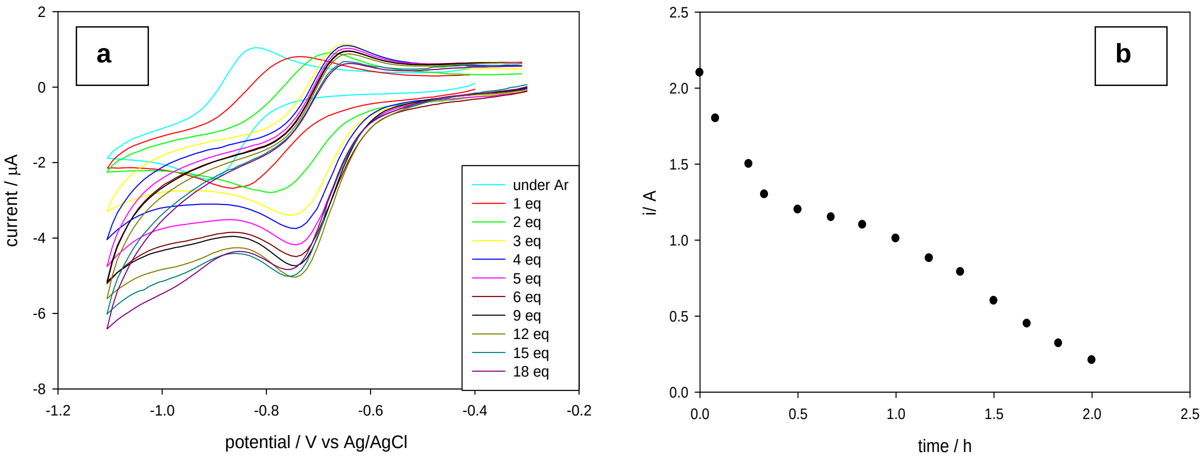

Fig. a) The cyclic voltammetry of $[Fe_4S_4(SPh)_4]^2$ at low concentrations of pentafluorothiophenol; b) The relationship between the current and time/h

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THE USE OF ENZYMES CULTURES OF FUNGI PENICILLIUM VERRUCULOSUM FOR HYDROLYTIC PROCESSING OF PEAT

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Vegetable raw materials are renewable and therefore the most perspective for the production biotechnology. In Russia the woods (coniferous and deciduous) and grain crops are considered as the main source of renewable raw materials. Larger territories of Russia are occupied with peat. Russia has huge resources of vegetable raw materials that especially promote biotechnology development.

The most significant productions based on bioconversion of vegetable raw materials are productions of alcohol, furfurol, proteinaceous feed additives, amino acids and others biologically the active materials [1].

The main constituent of vegetable raw materials are carbohydrate components – polysaccharides which quantity in different types of raw materials fluctuates from 40 to 75 %.

The enzymes catalyzing processes of splitting of polysaccharides before more prime connections with water participation fall into to a class of hydrolyzing enzymes, to be exact, to carbohydrases (amylases, cellulases, hemicelluloses, polygalacturonases, pectinases and others).

In Russia the commercial ferment medicine "AGROTSELL" which producer is the strain of a mushroom of Penicillium verruculosum is widely used. A principal component of this medicine is the cellulase participating in destruction of cell-like walls of plants by means of enzymatic hydrolysis the glikozide of communications of not starchy polysaccharides – first of all xylans (pentosans), and also β – glucans, and also other carbohydrases among which xylanases and pectinases most often occur. [2]. Characteristics of ferment medicine are provided in the table.

Table. Characteristics of the ferment medicine "AGROTSELL"

Name of indexes	AGROTSELL
Cellulose activity, piece/g, not less than	4000
β-glyukanaze activity, piece/g	3200
Ksilanaze activity, piece/g	1000
Spores of a mushroom of a producer and pathogenic microorganisms	are not allowed

In the real research experiments by determination of content of monosaccharides in peat by means of enzymes of culture of fungi Penicillium verruculosum which is a part of the medicine "AGROTSELL" were made. Riding peat of 30 % of humidity and 15 % of extent of decomposition was for this purpose used, peat was selected from the field the Vasilyevsky moss, Kalininsky district, the Tver region.

Data of an experiment showed that there is a gradual accumulation of a monosaccharide over all experiment. In a hydrolysate of peat 12 mg of glucose in 29 clocks of carrying out process collected that is not a limit for this process. In further experiments it is planned to increase time of carrying out experience to obtain more complete data on this process.

Thus, relevance of further researches consists in the subsequent definition of the reducing substances in wider time slice for the purpose of receiving the maximal exit of monosaccharides by means of ferment systems of various cultures of microorganisms.

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CONTROLLED FABRICATION OF CATALYSTS FOR GREEN CHEMICAL PROCESSES

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Our catalytic studies highlight the effects of support and gold particle size in electrocatalytic applications (glycerol oxidation) and initiator-/solvent-free aerobic oxidation of cyclohexene [1-7]. More recently we have demonstrated that green catalytic process of aerobic oxidation of amines to nitriles can be driven by the visible light using hydrous ruthenium oxide nanoparticles on TiO_2 [8]. We have developed series of catalysts based on clusters and/or bio-templated titania which show promising activity in hydrogen production and CO_2 hydrogenation.

We also performed a range of fundamental studies on these materials [9-17]. The detailed DFT studies of the ligated clusters allowed systematic identification of bands observed in the far-IR spectra and interpretation of the ultra-high resolution electron microscopy images of clusters supported on titania nanosheets. Synchrotron XPS studies of pure and supported clusters reveal their unique electronic properties and highlight the importance of support chemistry in controlling aggregation of clusters. We also used ultra-high resolution TEM and AFM/STM to study supported clusters on titania.

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ORAL PRESENTATIONS

Section V. CATALYSIS FOR ENVIRONMENT AND SUSTAINABILITY

Catalytic processes for energy efficiency and ecology
Catalytic processing of waste

CO_2 UTILIZATION VIA AUTO-THERMAL CATALYST-ASSISTED CHEMICAL LOOPING

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Carbon dioxide, a major green-house gas, has become an attractive source of carbon for the chemical industry owing to its low cost and high availability. Valorizing CO_2 towards useful chemicals is particularly interesting from both environmental and economic point of view [1]. Cyclic conversion through Catalyst-assisted Chemical looping Dry Reforming (CCDR) over a bifunctional bed composed of a physical mixture of a Ni-based reforming catalyst and a Fe-based oxygen storage material (OSM) is a novel technology for CO_2 utilization [2]. In this process, a given reaction is divided into two half-cycles: (1) CH_4 and CO_2 are first converted over Ni into H_2 and CO which reduce Fe_3O_4 to metallic Fe; (2) reduced Fe_3O_4 is regenerated via interaction with CO_2 resulting in CO production. Compared to the conventional dry reforming of CH_4, which produces syngas, CCDR is designed for maximized CO_2 conversion (three molecule of CO_2 per molecule of CH_4).

However, the overall CCDR process is strongly endothermic (ΔH_{298} = 330 kJ/mol), requiring high operating temperature and thereby leading to fast catalyst deactivation. Alternatively, the process could be rendered auto-thermal by co-feeding oxygen in close analogy to industrial auto-thermal CH_4 reforming. Here, a new process, auto-thermal catalyst-assisted chemical looping, is presented (Eq. 1).

$$\mathrm{CH_4 + xCO_2 + (3-x)/2O_2 \leftrightarrows (1+x)CO + 2H_2O} \qquad \text{(Eq. 1)}$$

Auto-thermal catalyst-assisted chemical looping integrates two strategies [3]: CO production through Fe_3O_4/Fe chemical looping and auto-thermal catalytic conversion of CH_4, O_2 and CO_2 to syngas over the Ni-based catalyst. A small amount of O_2 is co-fed with CH_4 and CO_2 to partially convert CH_4 in an exothermic reaction (partial oxidation or combustion), generating heat in-situ and thereby compensating the strong endothermicity of the reduction reaction.

A detailed study of auto-thermal catalyst-assisted chemical looping for CO_2 utilization was carried out using different reactor bed configurations composed of core-shell structured materials, such as Ni/Zr@Zr reforming catalyst, Fe/Zr@Zr OSM and Fe/Zr@Zr@Ni@Zr bifunctional material, all of which were synthesized by a combination of nanocoating and impregnation [4]. To optimize the efficiency of this process, the distribution of reforming catalyst and OSM was assessed based on the concept of double or single-mixed layer bed as well as the on a bifunctional material bed (Figure 1a), all of which were expected to work in different modes (Figure 1b).

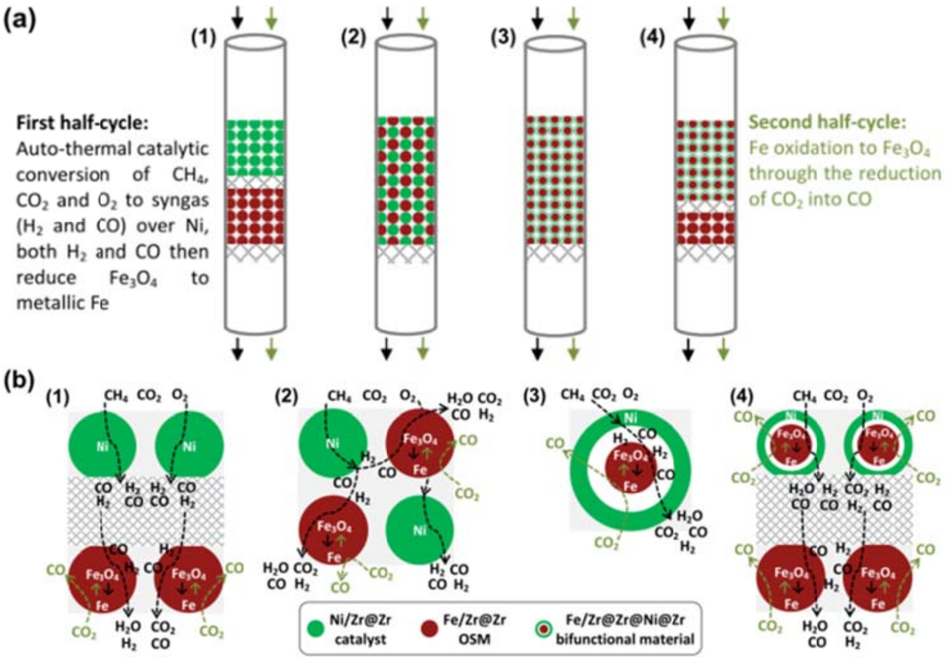

Figure 1. **(a)** Schematic representation of the auto-thermal catalyst-assisted chemical looping process for CO_2 utilization over different reactor bed configurations composed of core-shell structured materials and the corresponding work modes **(b)** during the whole process.

In-situ XRD characterization allowed to monitor the evolution of crystallographic phases of the materials during redox cycling. The morphological changes of materials were examined by STEM-EDX after 25 cycles. The double-mixed layer of Fe/Zr@Zr@Ni@Zr and Fe/Zr@Zr (Figure 1a-b4) exhibits highest CH_4 and CO_2 conversion to CO at the 750 ~ 900 °C, making it the most suitable configuration for the auto-thermal catalyst-assisted chemical looping process.

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Acknowledgements

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OP-V-2

EFFECT OF MORPHOLOGY OF NANOSTRUCTURED CERIA-BASED CATALYSTS FOR THE OXIDATION OF CO, SOOT AND NO

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In modern automotive catalysis noble metals are preferred catalytic materials for the abatement of pollutants. On the other hand, Ceria-based systems have received much interest because of their effective redox behavior and high oxygen storage capacity. Therefore, in this work we have focused our attention on the synthesis of various ceria nanostructures obtained by hydrothermal procedure [1,2]. Different pH and T values were used to obtain various textural and structural properties, as shown in Figure 1. The physico-chemical properties of the materials have been investigated by complementary techniques. Then, the catalytic activity of the prepared materials was tested for CO, NO, soot and NOx-assisted soot oxidation reactions

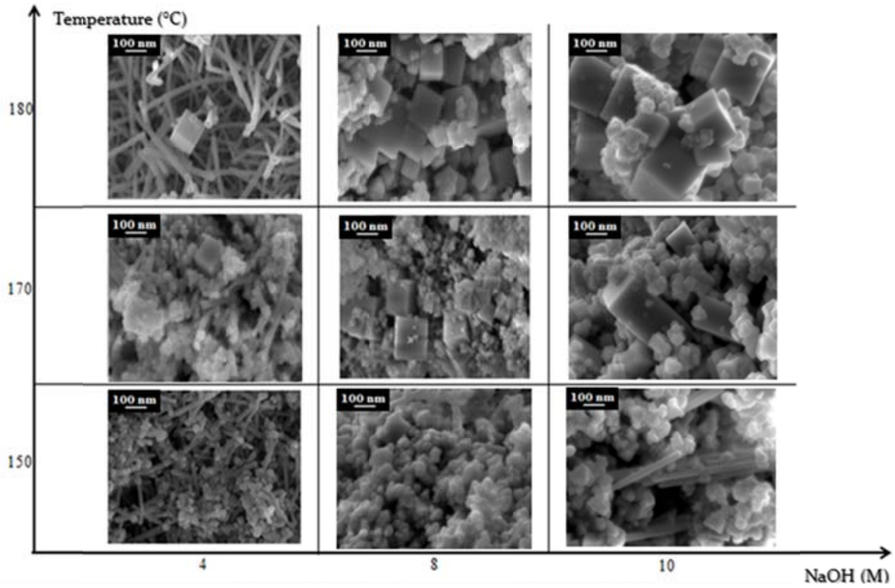

Figure 1. Ceria catalysts prepared by hydrothermal synthesis at different temperature and NaOH concentration values

The results have shown that for the oxidation of soot, the best catalyst exhibits the highest contact with particulate itself. On the other hand, for both the NO and CO oxidations the activities depend on multiple effects related to structural properties (i.e. lattice defects).

A similar study has been carried out with Ce-Cu nanostructured materials to investigate both the structural and electronic features effects on the catalytic activity.

The catalysts are synthesized by the hydrothermal technique [1,2] using different atomic percentage of Cu (namely $Ce_{0,975}Cu_{0,025}O_2$ with 2,5 % at., $Ce_{0,95}Cu_{0,05}O_2$ with 5 % at., $Ce_{0,9}Cu_{0,1}O_2$ with 10 % at.). In Figure 2 are shown the TEM images of these catalysts.

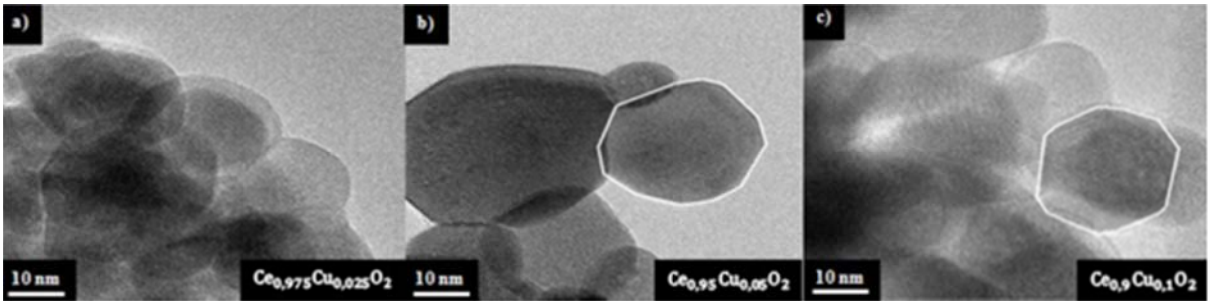

Figure 2. TEM images of sinthesyzed copper-ceria based catalysts.

As shown in Figure 2.b and 2.c we obtained well defined nanostructures (polyhedra). These nanocatalysts were tested for the dissociation of N_2O: the results shown that these catalysts are more reactive than those ceria-based.

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EVALUATION OF CATALYST DEACTIVATION DEGREE IN THE PROCESS OF DIESEL FUEL DEWAXING

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Deactivation of the dewaxing catalyst leads to necessety of the process temperature increase, according to the catalyst activity (Table 1). This results in decrease in the yield of the target diesel fraction, increase in the yelds of naphtha fraction and residue (Table 2).

Table 1. Evaluation of catalyst deactivation degree in the process of diesel fuel dewaxing over 2012–2016 years period (full scale experimental data)

2012 year					
Date	Feedstock flow rate, m^3/h	T (in dewaxing reactor), °C	Yield of diesel fraction, %	Liquid product yield, %	CFPP (diesel fraction), °C
29.03.12	327	337	58.2	88	–27
2014 year					
26.03.14	323	354	51.9	87	–27
2015 year					
05.01.15	321	352	50.7	90	–27
2016 year					
15.08.16	320	355	50.7	90	–26

Table 2. The yield of fractions in the process of dewaxing over 2012–2016 years period (full scale experimental data)

Year	2012	2013	2014	2015	2016
Yield of diesel fraction, %	74 – 90	63 – 88	52 – 65	54 – 60	44 – 52
Yield of naphtha fraction, %	8 – 10	10 – 12	15 –18	18 – 20	20 – 21
Yield of residue >340 °C, %	5 – 15	10 – 25	25 – 30	30 –35	35 – 40

According to the full scale experimental data the catalyst activity by the 2016 year comprised:

$$Akt = \frac{\Delta - \Delta T}{\Delta} = \frac{60-19}{60} = 0.68$$

Therefore, catalyst deactivation degree comprised 32 % over the given operation cycle.

This research uses the non-stationary mathematical model for solution to a problem of catalyst deactivation forecasting and optimization of the process operating conditions depending on the changing feedstock composition and the demand for diesel fuel components of the certain grade (summer, winter or arctic grade).

$$\begin{cases} G\cdot\dfrac{\partial C_i}{\partial z}+G\cdot\dfrac{\partial C_i}{\partial V}=\sum\limits_{j=1}^{m}a_j\cdot W_j \\ G\cdot\dfrac{\partial C_i}{\partial z}+G\cdot\dfrac{\partial T}{\partial V}=\dfrac{1}{\rho\cdot C_p^{CM}}\sum\limits_{j=1}^{m}Q_j\cdot a_j\cdot W_j \end{cases}$$

Where z is the total volume of processed feedstock date of fresh catalyst load (m^3); G is the feedstock flow rate (m^3/h); C_i is i^{th} component content in the feedstock (mol/m^3); V is the volume of catalyst bed (m^3); a_j is the catalyst activity in j^{th} reaction; ρ is the density of the mixture (kg/m^3); $C_p{}^m$ is the specific heat capacity of the mixture (J/kg·K); Q_j is the heat effect of j^{th} reaction (J/mol); T is the temperature (K); W_j is the rate of j^{th} reaction; m is the number of reactions.

Using the mathematical model the optimal temperature was determined for two feedstock compositions so that the product CFPP is equal to –26 °C and the yield of the product is equal to 86 %. The feedstock compositions are presented in Table 3.

Table 3. Fedstock compositions and technological parameters

Feedstock composition			Operational parameters	
Boiling points, °C	Feedstock-1	Feedstock-2	Parameter	Value
			Feedstock composition, m^3/h	280
10 %	256	263	Quench of H_2-gas, m^3/h	15000
50 %	307	314	Pressure, MPa	6.799
90 %	360	353		
Density at 20 °C	852	831		
N-paraffins, wt.%	16.10	21.24		

The results of calculation are presented in Fig. 1 and Fig. 2.

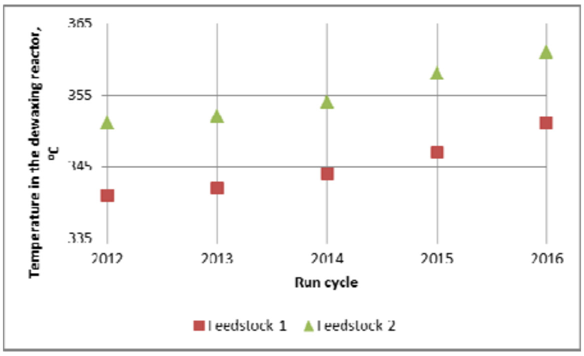

Fig. 1. Temperature in the dewaxing reactor depending on the feedstock composition and catalyst activity

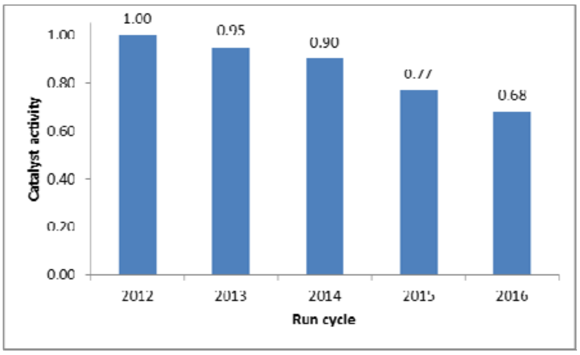

Fig. 2. Dewaxing catalyst activity

Therefore, increase in the process temperature over the period 2012-2016 years due to deactivation comprised 10 °C.

THE MESOPOROUS FIBROUS ALUMINA SUPPORTED TRANSITION METAL-BASED MATERIAL: SYNTHESIS, STRUCTURE AND CATALYTIC PROPERTIES IN CARBON DIOXIDE METHANATION, METHANE STEAM REFORMING AND DEEP OXIDATION REACTIONS

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Abatement of waste gases containing harmful VOCs is an environmentally important task, and one of the most efficient and economically feasible VOC removal technologies is catalytic combustion. However, global warming caused by evolution of huge amount of carbon dioxide has become a challenging problem. Recycling of carbon dioxide enables not only to prevent global warming but also to supply useful low-carbon fuels. The catalytic hydrogenation of CO_2 into fuels such as methane, methanol, dimethyl ether, syngas is a promising recycling approach which opens new concepts and opportunities for catalytic and industrial development.

In this work, we focus on the preparation of a novel structured transition metal-based catalyst hosted on alumina nanofibers (ANF) by both conventional techniques and recently developed template-assisted wet-combustion synthesis method [1-3]. In order to prepare nickel-based catalyst, the alumina nanofibers were wetted by a reactive solution containing the metal precursor and organic fuel, followed by the heat treatment until self-ignition and combustion-synthesis of the desired material (Fig. 1). The organic fuel was supposed to act as metal dispersing and complexing agent, and provide homogeneous distribution of metal precursors throughout the alumina. Furthermore, large amount of gases evolved under combustion enabled to synthesize nano-sized material, denoted as Ni/ANF(F), with improved catalyst textural properties without further calcinations. Copper- and platinum based catalysts (Cu/ANF and Pt/ANF) were synthesized via incipient wetness impregnation and adsorption from the solution, which is accompanied by strong precursor interaction with the support to form metal species of atomic dispersion after further calcination. The catalysts were characterized by BET, XRD, XPS, TEM, EDX, SEM, TPR and TPD techniques.

OP-V-4

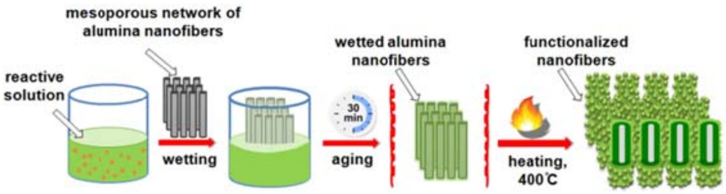

Figure 1. Schematic steps of the wet-combustion synthesis

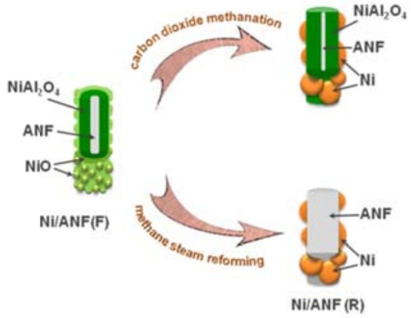

Figure 2. Schematic view of the single fiber after CDM and SRM reactions

The carbon dioxide methanation (CDM) experiments were performed at temperatures 275-425 °C using the following gas feed composition: 8.2 vol. % CO_2, 38.2 vol. % H_2 and 53.6 vol. % Ar. Total feed flow rate was adjusted to WHSV of 34000 $scm^3g^{-1}h^{-1}$.

The steam reforming of methane (SRM) experiments were performed at temperature of 700 °C using the conventional model gas feed composition with molar ratio $H_2O/C = 2$: 33.3 vol. % CH_4 and 66.7 vol. % H_2O. Total feed flow rate was adjusted to WHSV of 45000-135000 $scm^3g^{-1}h^{-1}$. The used catalysts after CDM and SRM reactions were denoted as Ni/ANF(M) and Ni/ANF(R).

The deep VOC oxidation was carried out at 150-350 °C using the following gas feed composition: 1.0 vol. % benzene, 0.5 vol. % O_2 and 98.5 vol. % He and 0.17 vol. % ethyl acetate, 20 vol. % O_2 and 79.83 vol. % He, and total feed flow rate GHSV = 2000 and 10000 h^{-1}, respectively.

Ni/ANF exhibited sufficient activity in carbon dioxide methanation and excellent activity in steam reforming of methane, conventionally catalyzed by the Ni-based systems (Fig. 2). Cu/ANF and Pt/ANF were more active and selective in deep benzene and ethyl acetate oxidation, respectively, compared with commercial alumina-based catalyst. Advanced performance of ANF-based catalysts can be associated with low density of the material, high gas permeability, high metal content and its uniform distribution on the support surface. Material is stable under the reaction conditions, keeping unchanged fiber-type structure and preventing nanoparticles sintering.

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MnO_x-TiO_2 CATALYSTS FOR NO_x SCR AT LOW TEMPERATURE

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Nitrogen oxides are by-products emitted by stationary and mobile sources in high-temperature combustion and constitute well-known atmospheric pollutants that can contribute to the ozone depletion, acids rains, photochemical smog and greenhouse effects [1]. Selective Catalytic Reduction (SCR) is considered a very effective and established technique for the abatement of nitrogen oxides (NO_x). It allows converting NO_x into nitrogen (and water) by introducing ammonia (or urea) in the exhausted gases, but it suffers low-temperature operation, urban driving conditions and improper calibration of urea dosage. The current commercial catalysts (e.g. V_2O_5/TiO_2) show high activity and selectivity in the temperature range 300-400 °C. It follows that a further considerable research effort for SCR catalysts efficient at low temperatures is required.

Manganese oxides-based catalysts have been studied in the last years for NO_x-SCR because of their versatility, eco-compatibility and the presence of labile oxygen species. They showed excellent low-temperature performance in the SCR of NO_x with ammonia, both unsupported and loaded on different supports [2-3].

In the present study, manganese oxides supported on rutile titanium oxide were investigated as catalysts for low-T SCR. Two different MnO_x percentage were deposed on rutile TiO_2 by means of Incipient Wetness Impregnation method. Catalysts were characterized and tested in the SCR process at different operating conditions.

MnO_x was deposed on commercial rutile TiO_2: the catalysts were prepared with the Incipient Wetness Impregnation (IWI) method by using Manganese(II) nitrate $Mn(NO_3)_2$ tetrahydrate as precursor. The catalyst powders, after grinding in an agate mortar, were calcined in air for 1h to remove the nitrate ions.

In order to verify the chemical and physical properties of the obtained materials, the catalysts were characterized. The phase structures of the samples were characterized by X-ray powder diffraction (XRD). H_2 temperature programmed reduction (H_2-TPR) analysis was performed using an analyzer equipped with a TCD detector. Multi-point BET surface area and pore volume of catalysts were measured via N_2 physisorption at 77 K. Morphology was observed by a Field Emission

Scanning Electron Microscope (FESEM). In order to verify real amount of deposed metal, ICP-MS apparatus was used. The catalytic activity of the prepared catalysts was analyzed feeding a gas mixture, composed by 400 ppm NO, 400 ppm NH_3, 2 % O_2 and He to balance, to a catalytic fixed-bed micro reactor. The gas hourly space velocity (GHSV) through the catalytic bed was about 70000 h^{-1}. The NO_x concentration was analyzed by means of a NO/NO_2 UV Limas gas analyzer, whereas the NH_3 concentrations in a Uras nd-IR gas analyzer. The outlet gas stream composition was monitored as a function of the bed temperature, increasing from 80 to 350 °C.

The curves of the catalytic activity in terms of NO and ammonia conversion are illustrated in Fig. 1.

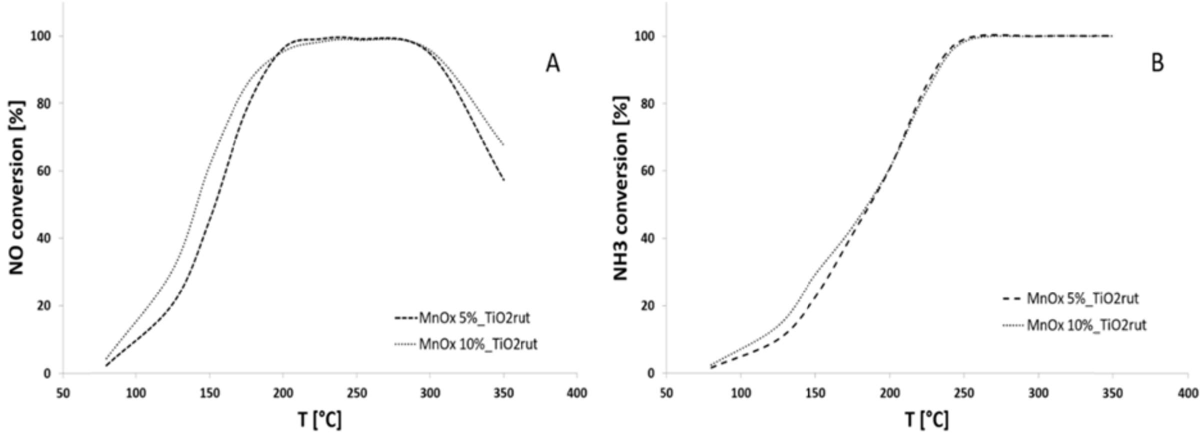

Fig. 1. SCR catalytic activity: NO conversion (A) and NH_3 conversion (B)

In general, the two catalysts showed similar behavior, meaning that conversion was not particularly influenced by increasing deposed MnO_x concentration. As concerns NO, complete conversion was reached at about 200 °C and was maintained for a large temperature range (about 100 °C) for both the catalysts. Ammonia conversion was complete at 250 °C. At lower temperature, performance of the catalyst with higher MnO_x concentration was slightly better for both NO and NH_3 conversions.

In conclusion, MnO_x supported on rutile titania appeared very promising for SCR catalytic reaction, as complete conversion of NO and NH_3 was reached at relatively low temperature.

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CO PROX ON Pt-M AND Pt-MO_x (M = Fe, Ni, Co) MODEL CATALYSTS: THE ORIGIN OF SYNERGETIC EFFECT

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The use of supported alloy nanoparticles is a promising way to modify activity and selectivity, improve stability or at least partially substitute expensive noble metals in conventional supported metallic catalysts, such as Pt-, Pd- and Rh-based systems. One of the reactions in which the properties of conventional Pt-based catalysts are needed to be improved is CO preferential oxidation (CO PROX) − a case of substrate-selective oxidation of CO in a huge excess of H_2. The CO PROX is considered as a promising way for deep CO removal from hydrogen-rich gas mixtures for proton-exchange membrane fuel cells (PEMFCs) feeding. PEMFC-based power-units are considered as green energy sources for distributed energetics. A number of Pt-M (M = Co, Ni, Cu, etc.) bimetallic systems showed a remarkable synergetic effect in CO PROX compared to Pt. However it is yet unclear whether the electronic effect of Pt-M interaction ("ligand effect") or Pt-MO_x interface ("ensemble effect") causes the synergism. In order to distinguish it, we have synthesized and studied the CO PROX performance of the unsupported phase-pure model catalysts with $Pt_{0.5}M_{0.5}$ (M = Fe, Co, Ni) solid solution and Pt-MO_x metal-oxide composite structures.

Fig. 1 illustrates the effect of temperature on the CO conversion (X_{CO}) and selectivity (S_{CO}) for CO PROX over the Pt, $Pt_{0.5}Co_{0.5}$, $Pt_{0.5}Ni_{0.5}$ and $Pt_{0.5}Fe_{0.5}$ catalysts. It is clearly seen, that the addition of second metal dramatically enhances the activity of Pt towards CO oxidation providing high activity at near-ambient temperatures in CO oxidation. The activity increases in the order $Pt_{0.5}Co_{0.5} \geq Pt_{0.5}Ni_{0.5} > Pt_{0.5}Fe_{0.5} >> Pt$. The same order remains for Pt-MO_x catalysts. For bimetallic samples catalysts S_{CO} is close to 100 % at low temperatures while $X_{CO} < 100$ %. In other words while CO is present in the reaction media the catalysts do not oxidize H_2. This fact indicates the dense coverage of Pt surface by adsorbed CO, that inhibits hydrogen oxidation. Hydrogen oxidation starts only at a temperature where the high CO conversion is reached and Pt surface becomes accessible to H_2. This results in sharp S_{CO} decrease at elevated temperatures. The observed phenomena is also pronounced for Pt-MO_x systems.

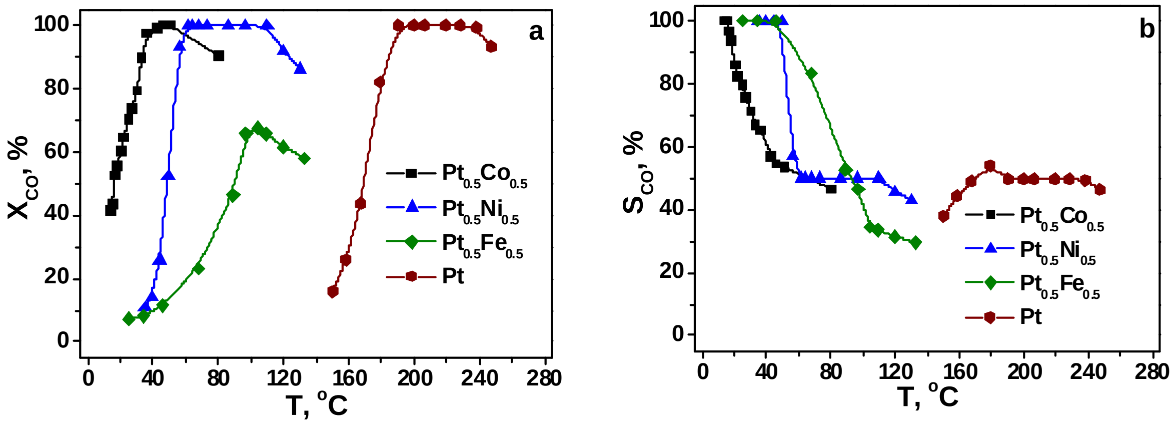

Figure 1. CO conversion (a) and selectivity (b) temperature dependences for CO PROX on Pt, $Pt_{0.5}Co_{0.5}$, $Pt_{0.5}Ni_{0.5}$ and $Pt_{0.5}Fe_{0.5}$ nanopowders. Feed gas (vol. %): 1 CO, 1 O_2 and H_2-balance. WHSV: 80000 $cm^3g^{-1}h^{-1}$

Most likely, the advanced properties of bimetallic systems are associated with bifunctional nature of $Pt_{0.5}M_{0.5}$ and Pt-MO_x catalysts. Probably, Pt is responsible for CO activation, the second metal is responsible for O_2 activation and the reaction takes place at the Pt-M or Pt-MO_x interface. This hypothesis explains the high selectivity of Pt-Ni and Pt-Co systems at low temperatures and exhibits the important role of “ensemble effect” in the synergism not denying the influence of “ligand effect”, which needs further investigation to be clarified.

The physicochemical properties of $Pt_{0.5}M_{0.5}$ and Pt-MO_x systems were studied by a number of techniques, including *operando* XRD, TEM, XPS and etc, and were correlated with catalytic performance.

Summarizing, for the first time the phase-pure $Pt_{0.5}M_{0.5}$ (M = Fe, Co, Ni) solid solution and Pt-MO_x metal-oxide composite model catalysts were synthesized and evaluated in CO PROX. The remarkable synergetic effect of second metal (Fe, Ni, Co) addition was observed. The synergism was associated with bifunctional nature of $Pt_{0.5}M_{0.5}$ and Pt-MO_x catalysts and reaction occurrence at Pt-M interface.

Acknowledgements

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GROWTH OF GRAPHITIC CARBON NITRIDE NANOSHEET ON TiO_2 MESOPOROUS SPHERES WITH HIGHLY IMPROVED PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION

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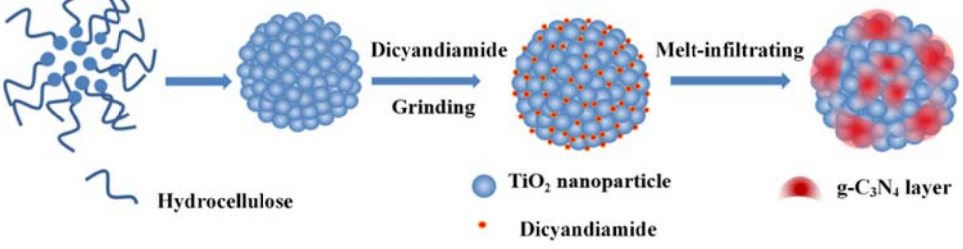
Harvesting solar light by semiconductors for production of green energy [1, 2], wastewater treatment [3, 4] and solar cell [5, 6] is considered as a promising solution to address the imperative energy and environment issues. Growth of graphitic carbon nitride on mesoporous TiO_2 spheres with well-controlled structures was achieved by melt-infiltrating dicyandiamide (DICY), as shown formation mechanism (Scheme 1). In particular, melting of a precursor of g-C_3N_4 into a mesoporous TiO_2 (M-TiO_2) enables growth of g-C_3N_4 with controllable coverage and thickness. The precursor of g-C_3N_4, DICY, can be melted at 190 °C and thus used to fill the mesopores of TiO_2. Subsequently, during carbonization of DICY, g-C_3N_4 could be controlled to grow on M-TiO_2 spheres. The melt-infiltration of DICY results in better fusion of g-C_3N_4 into M-TiO_2 and thus a strong interfacial connection between TiO_2 and g-C_3N_4, which are important in promoting both visible light adsorption and photo-generated electron transfer. TiO_2/g-C_3N_4 composites exhibited much higher photocatalytic activity than TiO_2 and g-C_3N_4 towards the degradation of Rhodamine B under both UV light and UV-vis light irradiation. The heterostructured combination provided a synergistic photocatalytic activity through an efficient electron transfer process. The factors affecting the photocatalytic activity were also discussed based on the result of structure analysis, optical and photoelectric characteristics, and photocatalytic reactions. This work provides a simple and effective method to reduce the barriers in composites to promote utilization efficiency of solar energy.



Scheme 1. Schematic illustration of the preparation of TiO_2/g-C_3N_4 microspheres

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CO_2 CONVERSION IN LIQUID HYDROCARBONS OVER Co NANOPARTICLES EMBEDDED IN METAL-ORGANIC MIL-53(Al) MATRIX

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A high concentration of CO_2 in atmosphere is a major ecological threat [1]. The conversion of carbon dioxide into carbon monoxide and methane is an effective solution of the of CO_2 utilization problem. Furtherly, CO and CH_4 may be converted in liquid hydrocarbons and valuable oxygenates according to Fisher-Tropsh synthesis (FTS) and hydroformylation. Especially, FTS is considered as one of the most prospective and economical ways to clean fuel production, because this heterogeneous catalytic process can produce a large variety of products such as paraffins, olefins, alcohols and aldehydes using syngas (CO and H_2) [2]. Supported Co nanoparticles are promising catalysts for FTS due to their activity and high selectivity to linear hydrocarbons combined with a low activity in the water – gas shift (WGS) reaction. The microstructure and FT performance of heterogeneous cobalt catalysts are affected very much by the support [3]. As the novel type of hybrid materials, metal-organic frameworks (MOFs) assembled by metal cations/metal oxide clusters and organic linkers) are now explored in catalysis, gas storage/separation, drug delivery, as sensors, and so on [4]. In particular, MOFs, have attracted significant attention as inorganic-organic host matrices for metal nanoparticles embedding due to their high surface areas, tunable pore sizes and tailored chemical properties, thus offering advantages over traditional microporous and mesoporous inorganic materials [5].

Our work deals with the preparation of the novel effective MOFs-based catalysts for carbon dioxide conversion in liquid hydrocarbons C_5-C_8 *via* two-steps process - CO_2 hydrogenation (500 °C, atmospheric pressure) followed by Fisher-Tropsh synthesis using carbon monoxide formed at the first step. Al^{3+}-derived microporous framework MIL-53(Al) (Al(OH)bdc, bdc = benzene-1,4-dicarboxylate) was selected as a host matrix for the Co nanoparticles deposition, because its exceptional chemical and thermal stability (as high as 520-550 °C). According to experimental results, novel Co/MIL-53(Al) nanohybrids display a behavior of bifunctional catalysts promoting both hydrogenation CO_2 into CO and FT synthesis. Conducting FTS reaction in 260-340 °C temperature range results in a formation of liquid hydrocarbons C_5-C_8 with process selectivity as high as 48 %.

The cobalt-containing catalysts were characterized by a combination of the physico-chemical methods: PXRD, STEM, oxygen titration, DRIFT spectroscopy and volumetric N_2 adsorption. XRD examinations confirm the retention of the crystallinity of the Co/MIL-53(Al) nanohybrids after two-step catalytic process. Both electronic microscopy and adsorption results indicate the Co nanoparticle localization mainly in the pores of the MIL-53(Al) matrix. The STEM study reveal the pronounced confinement effect of the metal-organic framework preventing the Co nanoparticles (around 5 nm) aggregation.

Thus, for the first time, carbon dioxide conversion in liquid hydrocarbons was carried out on the Co nanoparticles embedded in MIL-53(Al) matrix. Our results demonstrate the new opportunities of the MOFs–based heterogeneous catalysts exploitation in severe conditions of CO_2 hydrogenation and Fisher-Tropsh synthesis.

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STUDY ON MESOPOROUS-SUPPORTED CATALYSTS FOR SIMULTANEOUS CO_2 AND STEAM REFORMING OF BIOGAS

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Conversion of methane and carbon dioxide, which are two of the most abundant carbon-containing materials, into useful products is an important area of the actual catalytic research. The methane-CO_2 reforming (dry reforming) to produce syngas is a very attractive route to produce energy and valuable compounds. This reaction offers advantages over methane steam reforming to produce a H_2/CO ratio adequate for processes such as the production of higher hydrocarbons and derivatives [1]. The process is inevitably accompanied by deactivation due to carbon deposition. In order to reduce the carbon deposition, CO_2 reforming of methane with a feed gas containing steam has been suggested. Moreover, in the presence of steam, methane steam-reforming occurs simultaneously and thereby higher selectivity for both CO and H_2 can be achieved, and also the H_2/CO ratio of the product gas can be controlled [2,3].

Recently, the most widely used catalysts for CO_2 steam reforming reaction are based on Ni. However, many of these catalysts undergo severe deactivation due to carbon deposition. Noble metals have also been studied and are typically found to be much more resistant to carbon deposition than Ni catalysts, but are generally more expensive. Moreover, the silica SBA-15, which possesses larger pores and higher thermal stability, may be used as a promising catalyst support [4].

In the present study, 10 % Ni/SBA-15 and 0.5 % Rh/SBA-15 catalysts were prepared, and their performances over the reaction of combined carbon dioxide and steam reforming of methane were investigated.

Ordered mesoporous silica SBA-15 was synthesized in a spherical shape, according to the procedures reported by Hussain et al. [5], and used as catalyst carrier. The supported Rh and Ni catalysts were prepared with the Incipient Wetness Impregnation (IWI) method by using $Rh(NO_3)_3$ and $Ni(NO_3)_2 \cdot 6H_2O$ as precursor, respectively. The catalyst powders were calcined in air after impregnation. The catalysts were characterized by XRD, ICP-MS, CO_2-TPD, BET and FESEM analyses. The activity of the prepared catalysts was analyzed feeding a gas mixture, composed by CO_2, CH_4 and steam ($CO_2/CH_4 > 0.75 \div 1.5$, $H_2O/CH_4 \cong 1.5$), to a catalytic fixed- bed micro reactor containing the catalyst powder diluted SiO_2. The gas hourly space velocity (GHSV) was varied. The outlet gas stream composition was monitored in the temperature range from 500 to 900 °C. Before each activity test, catalyst was reduced in H_2 at 500 °C.

The first tests were carried out on both Ni and Rh supported catalysts at GHSV = 26000 h^{-1} and with CO_2/CH_4 ratio equal to 0.85. Results in terms of CH_4 conversion, H_2 yield and H_2/CO ratio are shown in Figure 1. The two catalysts reached similar methane conversion and H_2 amount produced was about comparable. Otherwise, H_2/CO ratio doubled with Rh based catalyst, meaning higher selectivity toward H_2 production. In particular, with 0.5 % Rh/SBA15 catalyst H_2/CO ratio was equal to 2, required value for the methanol synthesis.

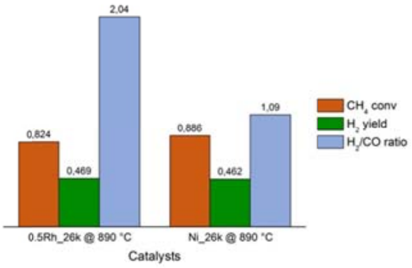

Figure 1. Comparison between Rh/SBA15 and Ni/SBA15

Deeper studies were performed on Rh/SBA15 catalyst by varying space velocity. Activity test at GHSV equal to 44000 and 15000 h^{-1} were carried out and performances were compared with those obtained at GHSV = 26000 h^{-1} (Figure 2). As expected, CH_4 conversion and H_2 yield decreased by increasing space velocity, but H_2/CO ratio was maintained about 2. In conclusion, two SBA15 supported catalysts (Rh 0.5 wt % and Ni 10 wt %) were tested for CO_2 and steam reforming reaction. SBA15 supported Ni showed high CH_4 conversion but poor H_2 yield and low H_2/CO ratio, that reached very promising value using Rh supported catalyst. By increasing GHSV on Rh/SBA15 catalyst, CH_4 conversion and H_2 yield was decreased but the H_2/CO ratio was maintained. In conclusion, SBA15 supported 1 wt % Rh was proved to be a promising catalyst over the reaction of combined carbon dioxide and steam reforming of methane.

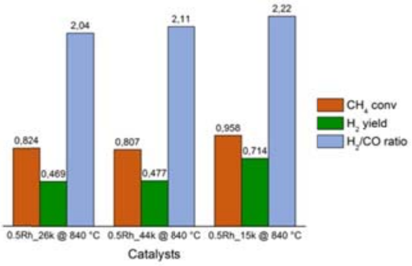

Figure 2. Performance of Rh/SBA15 and at different GHSV

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POSTER PRESENTATIONS

INVESTIGATION OF THE INFLUENCE OF ULTRAVIOLET AND ACOUSTIC EFFECTS ON THE PROPERTIES OF HEAVY OIL

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Experimental and theoretical studies of physical impacts influences on the distribution of heavy metals and viscosity of heavy oils are given in the article. The oil of Yaregskoye (Timan-Pechora province) oil field was chosen as the research object. Microinclusions of metals (V, Ni, Ti, Fe, etc.) in the mineral parts have been detected using scanning electron microscopy and electron microprobe analysis. In order to extract these metals, researches on influences of the extractant type and concentration on the extraction process was carried out. Types of extractants and time of ultrasonic treatment were evaluated. They allow the intensification of the extraction process flow. Cavitation-extraction scheme of metals extraction from high-viscosity oils on base of solvent deasphalting technology is suggested.

A lot of metals such as vanadium, nickel, silver and other are contained in the heavy oil. This allows us to consider heavy oil as a multipurpose complex of minerals. Destructive and non-destructive processes exist for the processing of heavy oil feedstock. They are aimed to the demetallization as well. The more common processes for the processing of heavy oils and oil residue (demetallization and obtaining of metals concentrate are happening simultaneously) can be divided into three:

- demetallization in the processes of oil preparation for transportation and processing,
- demetallization in petroleum refining processes,
- alternative processes of oil refining.

They are aimed to demetallization of petroleum feedstock using a variety of physical methods of influence. Alternative processes are accompanied by processes of adsorption and heterogeneous catalysis, for example, the process of solvent deasphalting [1-5]. In the frame of the proposed work, the research in the matter of valuable metals extraction for the heavy oil from the Yarega oilfield was carried out;

solvent deasphalting with addition of several physical impacts accompanying by absorption and heterogenous catalysis was applied.

Experimental and theoretical studies the physical impacts influences on the distribution of heavy metals and the viscosity of heavy oils are given in the article. Microinclusions of metals (V, Ni, Ti, Fe, etc.) in the mineral part have been established using scanning electron microscopy and electron microprobe analysis. Researches on the type and concentration of the extractant influence on the extraction process was performed to extract these metals. It was found that low-molecular organic compounds (kerosene and ethanol) have the greatest extraction ability. Ultrasound processing intensifies the extraction process. Cavitation-extraction scheme of extracting metals from high-viscosity oil was offered on the basis of experimental and theoretical studies [6-7]. The proposed scheme is designed on the basis of technology of solvent deasphalting, using reasonable extractants. It includes an extraction stage in an ultrasonic field with the separation of the insoluble fraction of asphaltenes in which a significant portion of the original heavy metals is concentrated.

Acknowledgements

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CATALYST FOR OBTAINING MOTOR FUEL FROM METHANOL

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Among the world trends in the development of chemistry is the improvement of the conversion of gaseous hydrocarbon raw materials into more convenient and environmentally friendly motor fuels and valuable chemical products due to the limited and depleted world oil reserves, as well as global environmental problems. One of them is the making of competitive, efficient and environmentally friendly fuels, an example of which is dimethyl ether (DME).

DME can be obtained from natural gas, using facilities for processing low-resource and low-pressure fields, which are not involved in commercial operation yet. DME supports fuel combustion without exhaust, a good cold engine start-up, noise reduction. The main advantage of DME as diesel fuel is environmentally friendly exhaust. The content of toxic components in it (without the use of catalytic exhaust gas processing) complies with the ecological requirements of European norms "Euro-3" and "Euro-4". You can also use DME in order to produce pure hydrogen for use in fuel cells - electrochemical generators of cars of the near future. The sphere of consumption of DME as an energy carrier gives a powerful stimulus for the deployment of its production on a large scale. And this, in turn, creates prerequisites for concentrating the efforts of researchers on the methods of its synthesis.

Currently, all options for the production of motor fuels from gas begin with the synthesis gas production process: carbon-containing feedstock ⇨ synthesis gas ⇨ methanol ⇨ gasoline. The transition from methanol to hydrocarbons occurs by dehydrating it first to DME, and then to hydrocarbons.

Now there are several ways to produce dimethyl ether. First, at a very high pressure and a high temperature, dimethyl ether and methanol are obtained from the synthesis gas. Another method is from methanol directly to obtain dimethyl ether. We conduct research in this direction, developed promising catalysts for the process of obtaining DME and hydrocarbons from methanol. The experiments were carried out on a flow-type installation at atmospheric pressure, in a temperature range of 250-500 °C, and a feed rate of 5-25 h^{-1} using alumina and zeolite-containing catalysts. Dependences of the yield of DME on the duration of the experiment and temperature were obtained.

We investigated bifunctional catalysts, which contain on the surface acidic centers for the hydration of DME and copper-containing centers for the methanol vapor conversion. The selectivity of the conversion of dimethyl ether to the target hydrocarbons is determined by the properties of the catalyst and the process conditions. As a result of the research, the most optimal catalytic systems and experimental conditions were selected, ensuring the production of dimethyl ether and hydrocarbons of various structures with high performance.

PP-3

ELECTROMAGNETIC INSTALLATION FOR NEUTRALIZATION OF WASTEWATER PRODUCTION OF OLIVE OILS

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The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation, flotation, absorbtion, and also methods of biological clearing. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil — 100 ÷ 1 mg/L
Final concentration of mineral oil — 0,5 ÷ 0,05 mg/L
Productivity on initial water — Up to 100 m^3/h
Operating mode — Continuous
Working temperature — 0 ÷ 50 °C
Working pressure — 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1) High efficiency;

2) Stability to a high level of pollution of communications (a rust, sand);

3) Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth);

4) Absence of a problem of deterioration in case of use the plastic reactor.

Installation has passed industrial tests in a zone: 1) Caspian pool: Russia, Republic Dagestan, 2006-2010; 2) Germany, Wesendorf and Hanover in 2015; 3) Greece, the Coast of the Ionian sea (Ligya) and the island of Corfu, 2015.

PHOTOS AND VIDEOS

Greece, the Ionian Coast. 2015. Test and presentation of the installation of water treatment of olive production to the technical quality of recycled water

Pilot Plant – Photo
Greece, the Coast of the Ionian sea (Ligya) and the island of Corfu, 2015

DEVELOPMENT OF ZEOLITE-LIKE MAGNETICALLY CONTROLLED CATALYSTS BASED ON ALUMINOSILICATE MICROSPHERES OF FLY ASH FROM THERMAL POWER STATIONS

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The most original and perhaps the most valuable components of fly ash from coal combustion from thermal power stations (TPS) are hollow aluminosilicate microspheres, which is a hollow, nearly perfect form silicate spheres with a smooth surface, with diameters from 10 to several hundred micrometers, an average of about 100 microns. The wall thickness from 2 to 10 microns, the melting temperature of 1400-1500 °C, the density 580-690 kg/m^3. The value of hollow aluminosilicate microspheres is determined by the fact that they are perfect fillers for a wide variety of materials.

Fractional separation of aluminosilicate cenospheres of fly ash TPS is carried on the developed by us laboratory installation in the upward vortex flow of the separation medium with superposition of multiple pulsation and the magnetic field of certain intensity. Using modern methods we studied the composition and structure of narrow fractions of definite composition, sorption properties of cenospheres optimal for obtaining a multifunctional porous materials in which the obtained powder and block materials with a regular porous structure.

Mossbauer studies of cenospheres have shown that in cenospheres with a content of more than 7 wt. % Fe_2O_3, iron forms part of two phases – defective magnetite (67 %) and a phase, in terms of parameters close to the disordered monticellite orthosilicate $(Ca, Mg, Fe)_2SiO_4$ (33 %). Defective magnetite at room temperature is in two magnetic equipartition states: ferrimagnetic and superparamagnetic. Magnetite sublattices are diluted by diamagnetic substitution. The diamagnetic dilution and the small size of the spinel formations lead to a superparamagnetic state and the destruction of fast electronic exchange between Fe^{3+} and Fe^{2+} ions in the *B*-magnetite sublattice.

Cenospheres with a lower concentration of Fe_2O_3 (3-4 wt. %) contain iron in the spinel (47 %) and orthosilicate (53 %). The spinel is in the paramagnetic state at room temperature. In silicate, iron in the divalent state occupies an octahedral position of the M2 type.

Based on the analysis of the results, the following features of the superparamagnetic phase of iron can be noted in comparison with magnetite:

– Mixed valence iron was not detected. Probably, the fast electronic exchange Fe^{3+} ↔ Fe^{2+}, characteristic of stoichiometric magnetite, is destroyed by the combined action of diamagnetic dilution and the defectiveness of small spinel regions;

– From the change in the populations of the iron positions with a decrease in the iron concentration in the cenospheres, it follows that Fe^{3+} cations enrich the tetrahedral sublattice, displacing Al^{3+} into an octahedral sublattice.

On the basis of microspheres separated from fly ashes of brown or black coal combustion at thermal power plants, we are developing technologies of modified catalysts preparation for: cracking of heavy fuel oil or heavy oil, allowing to receive from heavy fuel oil to 64 wt. % of light fractions, including 14.5 % of gasoline, and up to 85 % of light fractions from heavy oil, including 37 % of gasoline fraction; hydrocracking, hydroconversion and hydroprocessing of hydrocarbon raw materials, allowing to bring the gasoline output with an octane number of 83.1 to 54.2 wt. %; paraffins dehydrogenation in the fluidized bed, which makes it possible to obtain at 580 °C up to 54-55 wt. % isobutylene from isobutane and up to 37 % propylene from propane; ethylene polymerization, with polyethylene yield up to 1000 kg of polyethylene per catalyst gram; Fischer-Tropsch synthesis in a reactor with a suspended layer, with CO conversion above 80 % and the target hydrocarbon selectivity of C2-C4 + C5 is 94.4 wt. %; ethylene oxidative chlorination, allowing to obtain up to 98.4 wt. % of dichloroethane with an efficiency of C_2H_4 using to 93.8 wt. %; methanol oxidation to formaldehyde, allowing under optimal conditions to bring formaldehyde yield to 99.9 % with 100 % selectivity of methanol oxidation to formaldehyde; methane oxidative conversion, which allows increasing the selectivity of C_2-products formation to 67.4 %, with a methane conversion of 23.8 %, which corresponds to the best known catalysts of methane oxidative condensation process; microspherical catalyst for oil residues cracking, which makes it possible to increase the total yield of the distillate fractions to 58.0 wt. %, at a boiling point up to 350 °C, the yield of gasoline is up to 18 wt. %, octane number – up to 82.5.

REMOVAL OF THE INSECTICIDE METHOMYL FROM WATER TO MAGNESIUM-ALUMINUM-CARBONATE LAYERED DOUBLE HYDROXIDES

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1. Introduction

HDL is a mixed plate-like hydroxide of di- and trivalent metals. The structure is described by the leaves piling ($M(OH)_2$) which are the same as those of brucite. The trivalent metal presence leads to positive charged leaves. The electro neutrality assumes by the anion spices solvated bay water [1,2] present with in the leaves area [4] such as phases exist as minerals: hydrotalicites [Mg-Al], hydrocalumite [Ca-Al] the green rust [Fe^{+2} - Fe^{+3}].

Otherwise, these minerals are rare in nature where the clay materials are essentially cationic clay (phyllosilicates). In seventies, the Miyata [9] works about the soft chemistry synthesis of HDL permitted their development. There are so many combinations (metals and leaves) that is possible to vary the chemical and physical HDL properties which increase the catalysis interest [6]. In another hand, the strongest ionic exchange capacities (3 to 4 meq/g) very reative hydroxide area favorises the chemisorptions. The HDL give also the possibility to catch the chemical pollutants [3,4]. It has already proved that the treatment of polluted water by nitrates, phosphate or chromates is efficient. HDL also plays a role in supporting or catalyzing the reduction of chemical pollutants [6].

2. Experimental

2.1. Synthesis

All HDL have been prepared by co precipitated method at constant pH (S. Miyata, 1975) [5,7,9]. It consists to realize a controlled precipitation by alkaline solution which contains the salt of the two cations. So, the phase [Mg_2AlCO_3] has been synthesized at an ambient temperature by a progressive addition of $Mg(NO_3)6H_2O$ 0,5 M and $Al(NO_3)_3$, $6H_2O$ 0,25M solution and Na_2CO_3 2M and NaOH 1M solution in reactor contained 100 ml deionised and carbonate less water under magnetic shaking. The pH is maintaed constant to the value 10 ± 0.1 by the addition of NaOH 2M. After 24 H at 85 °C has been washed and centrifuged 3 times then let to dry at 65 °C.

PP-5

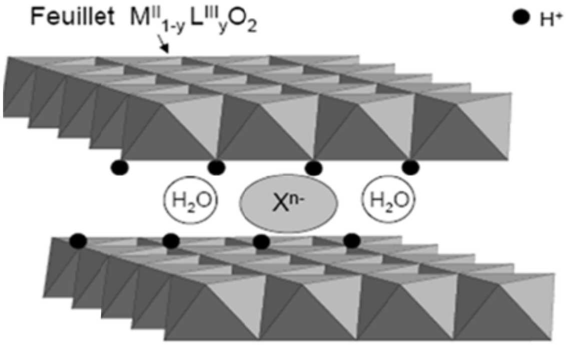


Fig. 1. Schematic representation of HDL

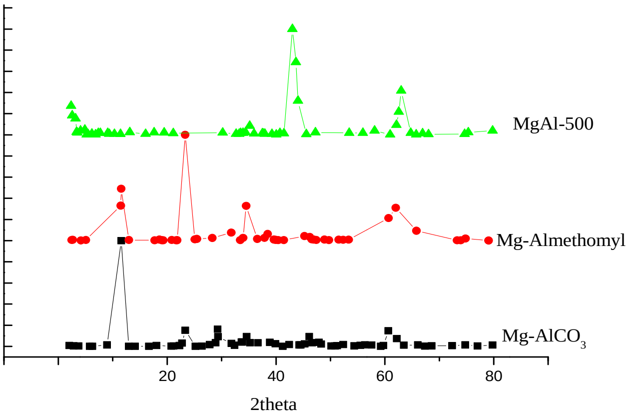
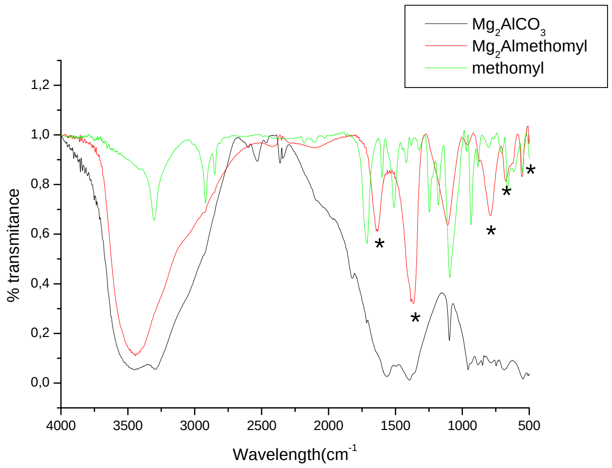


Fig. 2. XRD patterns of [MgAl-CO_3], [MgAl-methomyl], [MgAl-500]

2.2. Isotherme adsorption

The methomyl isotherme adsorption have been enregisted at 25 °C in a closed reactor under magnetic shaking. 10 mg of clay are dispersed in 25 ml of Methomyl solution of a variable concentration (C_i=2 to 6 mmol/L). After 24 h the solide has been sparated from the solution by centrifugation the Methomyl concentration is determined by UV visible spectrometer [Methomyl : λ = 254 nm].The isothermes concerned by the quantity of Methomyl C_S adsorbed by clay are represented in figure 4.



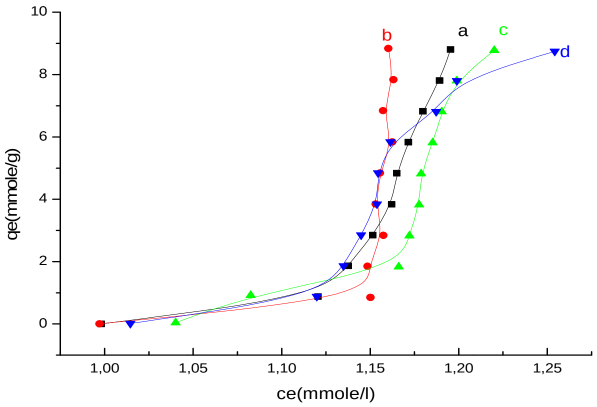


Fig. 3. Show the FT-IR includes the infrared spectra of HDL phases [Mg_2AlCO_3], [$Zn_2Al\ CO_3$], [Mg_2Al500]and patterns of the most representative

Fig. 4. Methomyl adsorption isotherms for (a) [Mg_2AlCO_3], (b) [Zn_2AlCO_3], (c) [Mg_2Al500], (d) [Mg_2Aledta], at 25 °C [Mg_2AlCO_3]

2.3. pH influence

The pH influence on the Methomyl adsorption by [Mg_2AlCO_3] has been examined. At pH < 5 the clay is partly dissolved. If the pH < 7 struggle with the carbonate anions is very probable [8,10S]. The figure 5 show that the maximum absorption at 5 < pH < 7 which correspond to natural water.

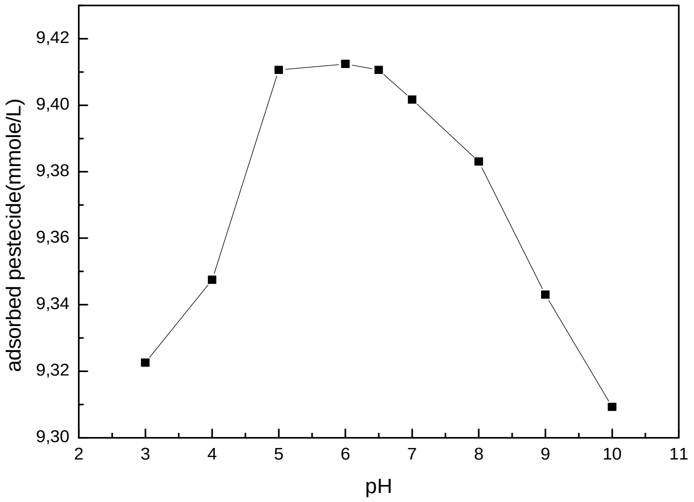


Fig. 5. Influence of the pH on Methomyl adsorption on [Mg_2AlCO_3]

3. Conclusion

The HDL offer to catch the organic pollutants. The Methomyl isotherm adsorptions are between type S and L this shows the moderate interactions between organic pollutants and clay. The absorption by exchange concerns first the surface then the whole solid. It depends on many factors: pH, charge density of leaver the clay morphology and solid / liquid.

Acknowledgments

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PP-6

ADSORPTION OF RHODAMINE B DYE ONTO EXPANDED PERLITE FROM AQUEOUS SOLUTION: KINETICS, EQUILIBRIUM AND THERMODYNAMICS

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Batch sorption kinetics of Rhodamine B (RB) by Expanded Perlite (EP) has been studied in terms of pseudo- first-order, pseudo-second-order and intra-particle diffusion models. The results showed that sorption process was best described by the pseudo-second-order model. The correlation coefficients R^2 obtained from pseudo-second-order model were higher than 0.97 under all the experiment conditions. The effect of initial dye concentration, contact time, solution temperature and pH solution on kinetic parameters are discussed. Thermodynamic studies and adsorption isotherms Langmuir, Freundlich and Temkin were used to describe this phenomenon of adsorption. The adsorption process was followed by UV-spectrophotometric technique in a specially designed adsorption cell. The results show that Expanded Perlite is a good adsorbent for the removal of Rhodamine B from aqueous solutions. The quantity eliminated was depended on the initial concentration, contact time, solution temperature and pH of solution.

Pd/C-PMHS BINARY SYSTEM AS A NEW APPROACH FOR BIO-OIL VALORIZATION

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The Bio-oil produced by pyrolysis of biomass has already shown potential to be considered sustainable and renewable energy source. However, high oxygen content and presence of phenolic compounds hinder the direct utilization of this promising product as a fuel. Therefore, further treatment is required in order to decrease the aromatic content. Many approaches have been proposed to improve the value of Bio-oil [1]. In this work an alternative Palladium on carbon-polymethylhydrosiloxane reducing system able to selectively hydrogenate Bio-oil model compounds into ketones is reported. The reactions were carried out by using THF/H_2O as solvent, Pd/C as heterogeneous catalyst and PMHS as hydride donor. These reaction conditions enable a selective hydrogenation of cresol isomers to the respective ketones. The presence of water is required since it contributes as a co-donor in the molecular hydrogen production [2]

No reaction was detected when Pd/C is absent. The hydrodearomatization of both *meta*- and *para*-cresols reached full conversion and 95 % selectivity to the corresponding ketone. The *orto*-cresol shows a lower reactivity due to the steric hindrance caused by the vicinal methyl group, which makes the molecule less prone to be stabilized by the Pd surface as shown by Liu et al.[3].

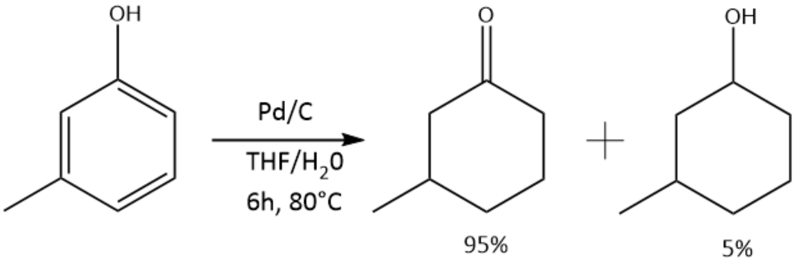

Figure 1. Reaction scheme of meta-cresol hydrodearomatization

Using the procedure proposed herein, all the cresol isomers can be hydrogenated with good yields and selectivity, with the only exception of *orto*-cresol. As the hydrogen used by the reaction is produced in situ, pressurized hydrogen is not required which makes the process safer. Furthermore, the use of PMHS provides an improvement from environmental point of view since it is a residue coming from the silicon industry [4].

Further investigation is ongoing on the applicability of these conditions to other classes of Bio-oil model compounds.

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PHOTOCATALYTIC DEGRADATION OF THIOPHENE DERIVATIVES ON TiO_2

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Keywords: Thiophene derivatives, maximum absorbance wavelength, ultraviolet, photocatalysis, TiO_2.

This study investigated the photocatalytic degradation of thiophene derivatives under UV light, taking thiophene as target material and using TiO_2 as catalyst [1]. From the characteristic analyses, the maximum absorbance wavelengths for the studied compounds were determined experientally. The results proved that the photocatalytic degradation increased with the maximum absorbance wavelength as expected.

This useful scientific information is discussed and correlations are established.

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PP-9

ENHANCEMENT OF THE ACTIVITY OF TiO_2 – BASED CATALYSTS BY DOPING WITH NOBLE METALS, INVOLVING OZONE IN PHOTOCATALYTIC DEGRADATION OF ADIPIC ACID

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Palladium and gold modified titania in the presence of oxygen and ozone containing mixture upon UV-A and UV-C irradiation were examined for their catalytic activity towards photodegradation of adipic acid (at 20 °C and atm. pressure). The samples were synthesized by extractive-pyrolytic method with 0.5 % loading of the active metal having particles size varying from 5 to 18 nm. The XRD, TEM and BET were employed for their structural and chemical characterization. In the presence of oxygen under UV-A light the apparent first-order rates constants of palladium and gold modified TiO_2 samples were respectively 1.7 and 2.3 times higher than that of the pure TiO_2 under same conditions. This higher conversion efficiency of the doped titania catalysts is due to the transfer of the ejected into the conduction band electrons of the TiO_2 to the LUMO of the noble metal as a consequence of the difference between reduction potentials of the TiO_2 and the noble metal which prevents the instant electron–hole recombination. Further, the effectiveness of the catalysts regarding to the photooxidation of adipic acid in the presence of ozone is greater both under UV-C and UV-A light for all samples tested. The reaction rate constants under 254 nm irradiation are about 3 times higher, relative to the irradiated with 365 nm light. This is due to the additional generation of $HO^{\bullet}$ radicals by the ozone on the conduction band of the TiO_2 photocatalysts as well as the result of O_3 photolysis by the UV-C light high energy photons.

Acknowledgements

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CATALYTIC ACTIVITY OF Ru-CONTAINING HALLOYSITE CATALYSTS IN HYDROGENATION OF AROMATIC COMPOUNDS UNDER TWO-PHASE CONDITIONS

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Halloysite is environmentally friendly, natural and cheap tubule nanomaterial available in thousand tons. Halloysite nanotubes are formed by 10-15 revolution of kaolin alumosilicate sheets and have diameter of 50-60 nm, a lumen of 12-15 nm and length of 500-800 nm. Halloysite surface is SiO_2 and the tube inside is Al_2O_3 which are oppositely (positive / negative) charged at pH range of 3-9 [1]. Due to its tubular structure, halloysite could be used as a container for stable metal nanoparticles and its side dependent chemistry make it a perfect material for modification.

In this work we compare two types of halloysite based Ru-nanocatalysts (Ru/halloysite; M-Ru/halloysite) with Ru nanoparticles assembled inside halloysite nanotubes in reaction of aromatic hydrocarbon hydrogenation under two-phase condition. Ru/halloysite was synthesized using pristine halloysite as a carrier and M-Ru/halloysite was synthesized using halloysite modified with cetyl trimethylammonium bromide. In both nanocatalysts Ru-nanoparticles were synthesized using Schiff base assisted metal salts intercalation techniques followed by in-situ reduction with $NaBH_4$ [2].

All samples were characterized by IR and ^{27}Al NMR spectroscopies, low-temperature adsorption/desorption of nitrogen and XPS techniques. The formation of metal nanoparticles in the internal cavity of halloysite was proved by TEM. Metal content was determined by X-ray fluorescence spectroscopy. According to XPS data, metal nanoparticles are preferably in the zero valent state.

Catalytic hydrogenation of aromatic compounds was carried out in a stainless steel 40 ml Parr batch reactor heated in a temperature-controlled oven. In a typical experiment, 250 μl of aromatic compounds (benzene, toluene and ethylbenzene) and 250 μl of water were placed to the reactor. Next, 5 mg of Ru/halloysite or

M-Ru/halloysite (metal content 1 % wt) was added. The reactor was sealed at the H_2 pressure of 3.0 MPa and heated to the reaction temperature (80 °C). Reaction time = 1 hour. Halloysite based catalysts showed high activity in the hydrogenation of aromatic compounds in the presence of water. It was shown, that aromatic compounds conversion under two-phase conditions on the Ru/halloysite catalyst is 88 % with 96-100 % selectivity of each product: cyclohexane, methylcyclohexane and ethylcyclohexane. It was shown, that M-Ru/halloysite catalyst is more active in hydrogenation of aromatic compounds with the presence of water. Thus, conversion of aromatic compounds is higher and is about 99 % while maintaining products selectivity.

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PALLADIUM DOPED MAGNETIC NANOCATALYSTS FOR SUSTAINABLE 5-HYDROXYMETHYLFURFURAL OXIDATION

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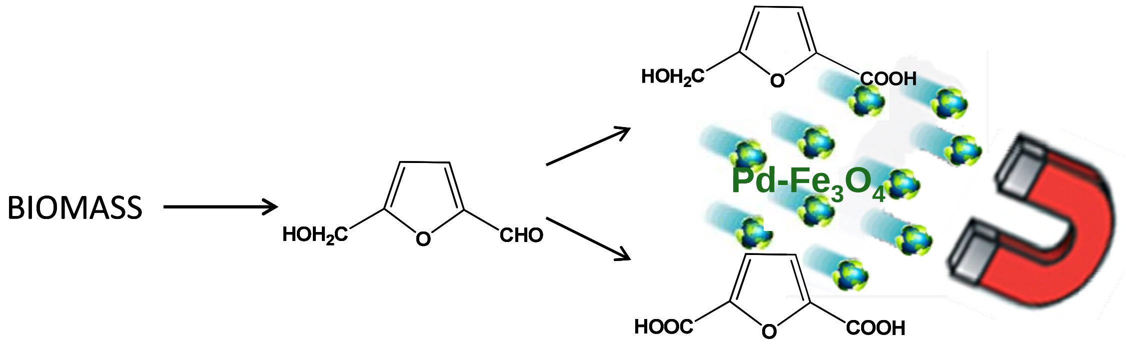
Diminishing reserves of the easily available petroleum resources and environmental impact of fossil fuels are the driving forces to the search of alternative energy and new carbon sources. Undoubtedly, carbon-containing molecules found in renewable biomass represent a sustainable feedstock for the chemical industry. Specifically furan compounds, such as 5-hydroxymethylfurfural (HMF) and its oxidation derivatives, have high potential for the production of chemicals and fuels. Moreover, their production from C_6-sugars affords high carbon profit and they are considered key platform chemicals in the biobased renaissance [1, 2]. For instance, 5-hydroxymethyl-2-furancarboxylic acid (HFCA) derived from the selective oxidation of the aldehydic moiety of HMF, serves not only as a monomer in the synthesis of various polyesters, but also shows antitumor activity [3]. Much more research interest has been devoted to the synthesis of 2,5-furandicarboxylic acid (FDCA) considered a top selected value-added chemical from biomass and a possible replacement monomer for terephthalic acid used to produce polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [4]. So, the aim of this study is the environmentally friendly synthesis of HFCA and FDCA through heterogeneously catalyzed reactions in water at mild conditions so as to guarantee a sustainable development. Pd doped Fe_3O_4 is proposed as easily recoverable and versatile catalyst being able to reach up to 86 % yields of HFCA when subjected to 10 atmospheres of O_2 and 60 °C in the as synthesized form. On the contrary, this catalyst can reach up to 70 % FDCA yields when working at 40 °C and atmospheric O_2 pressure in a mildly reduced form.

In order to design a truly sustainable process also from the economic point of view, biomass derived HMF raw liquors must be employed. The use of this type of liquors avoids complex, expensive and inefficient HMF purification processes, adjourning them to the refinement of the final product.

PP-11



Therefore, catalysts here proposed were also tested in a cascade process of biomass valorization using raw hydrolysates derived from cellulose. These aqueous liquors obtained by hydrolysis and dehydration with a solid acid contained mostly HMF and furfural as well as small amounts of unreacted sugars. Quite good results were obtained from the cascade process using Pd doped Fe_3O_4 leading to 81 % yield of HFCA, 4 % FDCA and 80 % yield of furoic acid (main furfural oxidation product). These preliminary results evidence the robustness of this catalyst and the high feasibility of this cascade approach.

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TETRAMER OF GOLD-PLATINUM AS A CATALYST FOR THE DEHYDROGENATION OF AMMONIA-BORANE

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Due to its ability to store large amounts of hydrogen (19.6 wt. %), ammonia borane (AB = $H_3N\text{-}BH_3$) is considered one of the main alternatives as future fuel carrier. One of the problems to be resolved about this substance is finding suitable methods to release its hydrogen at relatively low temperatures. Among some others, catalytic methods are very good alternatives.[1,2]

In this work we explore the use of the predicted more reactive gold-platinum tetramer cluster, the global minimum species of composition Au_2Pt_2,[3] as a catalyst for the dehydrogenation of AB. A systematic stochastic-based search[4] and subsequent gradient-based optimization of the AB-Au_2Pt_2 structures at high levels of theory, including relativistic effects for the Au and Pt atoms, gave an exhaustive scanning of the configurational space for the system. It was found that the AB molecule always interact with the Au_2Pt_2 clusters through the B-H unit of AB and the Pt atoms of Au_2Pt_2. The energy profile for the release and diffusion of hydrogen on the gold-platinum cluster, indicates that it is a favorable process from thermodynamic and kinetic point of views, and that occurs more easily than in the case of using Au_4.

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PP-13

$La_{1-x}Ca_xCoO_{3-\delta}$ PEROVSKITES FOR DEEP OXIDATION

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Due to high catalytic activity in oxidative processes, high mixed ionic (O^{-2}) and electronic conductivity at elevated temperatures $La_{1-x}Ca_xCoO_{3-\delta}$ perovskites have technological interests as materials for oxygen permeable membrane, electrodes in solid oxide fuel cell, oxygen sensors and catalysts for deep oxidation process. Preparation route may play a very important role in their properties due to influence not only on microstructure and defect structure of perovskites but on a phase composition as well. Among different routes for perovskite preparation Pechini and mechanochemical (MC) routes are of interests due to their energy efficiency and waste less.

The goal of the paper is preparation of $La_{1-x}Ca_xCoO_{3-\delta}$ oxides via Pechini and MC routes and investigation of their physical and chemical properties and catalytic activity in methane and CO oxidation processes that is very important for design of advanced catalytic system and catalysts for exhaust gas cleaning.

By Pechini route $La_{1-x}Ca_xCoO_{3-\delta}$ (x=0-1) oxides were prepared from appropriate nitrates taken in needed proportions. After their solution and mixing, ethylenglycole and acetic acid were added and then solutions were aged at 70-80 °C until resins were formed. Obtained precursors were calcined at 900 °C during 4 h. Synthesis by MC route was done using La_2O_3, Co_3O_4 and CaO oxides in needed proportions. After their MC treatment in the APF-5 planetary ball mill, powders were calcined at 1100 °C for 5 hours. The ratio of the weights of milling balls and oxide powders was equal to 10:1, acceleration achieved in the drums of the mill was ~ 40 g.

Catalytic activity in methane oxidation was studied with 0.25-0.5 mm particles in flow reactor in the range of 250-600 °C. Oxidation products were carbon dioxide and water. Samples before and after tests were studied with XRD, TEM, TA, H_2-TPR, BET.

According to XRD data formation of single-phase solid solutions in the range of $0 \le x \le 0.4$ was revealed for samples prepared by Pechini route although HRTEM revealed presence of admixtures of simple oxides as well. At x>0.4 the brownmillerite phase is additionally appeared. After catalytic tests in CH_4 oxidation phase composition and structure of the samples did not change significantly, but HRTEM indicates formation of nanoheterogeneity in perovskite particles. So $LaCoO_{3-\delta}$ perovskite with rhombohedral structure modification after test is characterized with appearance of clusters with orthorhombic structure modification. In the samples with x=0.2 and x=0.4 there is formation of planar defects in (101) direction of the crystallographic planes. As a result in $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ sample after test the areas with alternating layers of the perovskite and brownmillerite structures are formed probably due to surface layers decomposition.

According to X-ray data all prepared by MC route samples in addition to perovskite contain admixtures of Co_3O_4 and/or CoO phases. Increase in Ca content leads to change perovskite structural modification from hexagonal (x<0.4) to cubic (x>0.4). At that samples with x=0.4-0.7 may contain both perovskite structural modifications. Starting from x=0.6 admixture of $Ca_2Co_2O_5$ with brounmillerite structure is appeared while perovskites content is decreased. According to TEM data perovskite particles consist of the blocks, their size is varied from 100 nm up to 1 mkm, while Co_3O_4/CoO particles are of 10-50 nm and aggregated. In addition calcium and/or lanthanum oxides were detected in the samples as well.

According to H_2-TPR data Ca adding leads to increase total hydrogen consumption as well as consumption up to 500 °C that may be due to Co^{+4} formation, but its quantity is lower than calculated per x.

Catalytic activity in methane oxidation depends on the samples composition and preparation route. In prepared by Pechini samples Ca adding up to x=0.3 leads to increase activity and then at x≥0.4 to decrease. Probably that formation of vacancy ordered structure (braunmillerite layers and then phase) leads to decrease activity at x≥0.4. In prepared by mechanochemical route samples Ca adding leads to decrease the activity very probably due to surface segregation of CaO. So obtained activity row for prepared by Pechini route samples: 0.2=0.3>0.4=0.6>0>0.8=1 differ from that for samples prepared via mechanochemical route in which the highest activity possess the sample with x=0 probably due to Co_3O_4 surface segregation. Taking into account both data on samples activity and stability namely $LaCoO_{3-\delta}$ perovskite is the most promising for different oxidation processes in $La_{1-x}Ca_xCoO_{3-\delta}$ oxide samples.

Acknowledgements

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PP-14

EFFECT OF THE SUPPORT ON THE PERFORMANCE OF Ni/Pd BASED CATALYSTS IN DECOMPOSITION OF OZONE

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Ozone is widely used in the industrial and environmental processes such as semiconductor manufacturing, deodorization, disinfection and water treatment [1]. The residual ozone must be removed because on the ground level it is an air contaminant [2]. An effective method for purification of waste gases containing ozone is the heterogeneous catalytic decomposition [3]. A range of catalytic samples made by extractive-pyrolytic method and based on nickel and palladium nanoparticles supported on inorganic supports such as activated carbon, silica, alumina and aluminium oxide hydroxide were tested in the reaction of ozone decomposition. Kinetic experiments at dry and humid ozone decomposition over alumina supported Ni/Pd catalytic samples were performed at O_3/O_2 flow rates between 6.0 and 24.0 l h^{-1}. The properties of the catalysts were confirmed by using various characterization techniques as XRD, SEM and TEM.

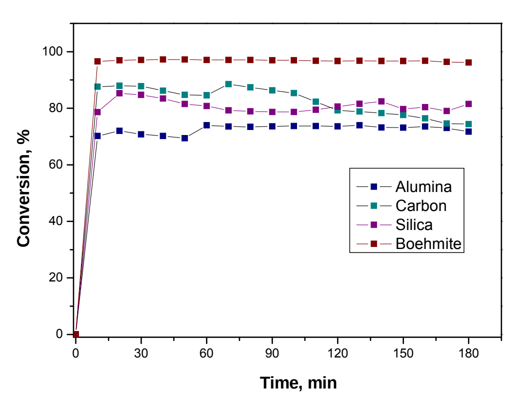

Fig. 1. Ozone conversion as function of ozonation time for the Ni/Pd catalytic samples denoted in graph legend

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GREEN CATALYTIC BIOREFINERY OF LARCH-WOOD BIOMASS WITH OBTAINING MICROCRYSTALLINE CELLULOSE AND FINE CHEMICALS

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The resources of larch-wood are large in the north regions of Russia, Canada and Europe. Meanwhile the larch-wood is little used for the production of pulp thanks to the high content of water-soluble substances and to the high density of wood. But the presence in larch- wood such biologically active substances, as flavonoid dihydroquercitin (QDH) and polysaccharide arabinogalactan (AG) makes appropriate the complex valorization of larch-wood biomass to produce bulk and fine chemicals.

This presentation describes the results of the study of larch-wood green biorefinery to produce fine chemicals, microcrystalline cellulose and enterosorbents.

Methods of ultrasonic, shock- acoustic, mechanochemical and steam – explosion impact are successfully used to intensify the AG extraction from larch-wood by the water.

Ultrasonic treatment of powdery wood during 0.5-1.0 min increases the yield of AG from 9.4-13.3 % mas. (conventional extraction at 95 °C) to 24.6-25.0 % mas. Shock-acoustic treatment of powdery wood allows to increase by 2.5 times the yield of AG, while reducing the temperature of extraction process from 95 °C to 25 °C and the extraction time from 120 min to 1 min.

It was shown that ethanol-water mixture extracts from larch-wood at the same time QDH and AG with high yields. The maximal yields of QDH (1.8 % mas.) and AG (19.0 % mas.) were achieved by extraction of larch-wood with 15 % ethanol during 2 h. Mechanochemical activation of wood shortens the time of QDH and AG extraction up to 30 min.

For valorization of extracted larch-wood the process of peroxide catalytic fractionation of wood on cellulose and soluble lignin in the medium of acetic acid – water was suggested to use. The activity of catalysts H_2SO_4, H_2MoO_4, $Fe_2(MoO_4)_3$ in this process was studied at 130 °C. It was found that the maximal activity has the catalyst 5 % H_2MoO_4, which allows to obtained with the yield of 40 % mas. the microcrystalline cellulose along with soluble lignin.

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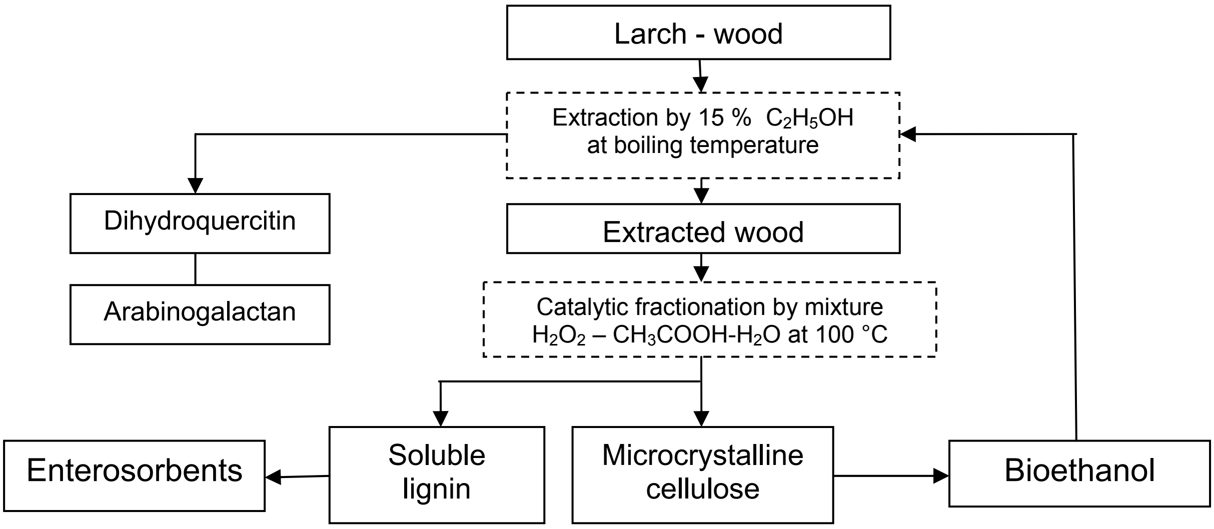
The method of preparing of effective enterosorbents from soluble lignin was developed. Obtained enterosorbents have the sorption properties similar to the commercial enterosorbents “Polyphepan”

Kinetic studies and optimization of the processes of larch-wood extraction by water-ethanol mixture and of extracted wood fractionation on MCC and soluble lignin in the medium “H_2O_2 – CH_3COOH – H_2O – catalyst H_2MoO_4” were carried out.

Yields of the products obtained from larch-wood at optimal conditions of wood extraction by 15 % C_2H_5OH and extracted wood peroxide catalytic fractionation (% mas. on a.d.w.): QDH – 1.8; AG – 19; MCC – 40, enterosorbents – 10.

Products of larch-wood biomass biorefinery were studied with the use of FTIR, solid state ^{13}C CP/MAS, XRD, SEM, elemental analysis and chemical methods.

The results of accomplished study allowed us to propose a scheme of green biorefinery of larch-wood with obtaining of QDH, AG, MCC and enterosorbents.



Acknowledgements

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MAGNETICALLY RECOVERABLE CATALYSTS FOR CELLULOSE HYDROGENOLYSIS

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Biomass-derived polyols are emerging as promising building blocks for value-added chemicals [1]. In particular, EG and PG, are important precursors for pharmaceuticals, liquid fuels, emulsifiers, and surfactants. The natural resource for the industrial production of these glycols is a fossil fuel, oil. An alternative pathway to EG and PG is cellulose catalytic hydrogenolysis in water. This reaction can be carried out as a *one-pot* process in subcritical water with various heterogeneous catalysts [2]. Ru-containing catalysts are considered to be the most active [3, 4]. Here, we describe successful one-pot syntheses of EG and PG from cellulose in a sustainable environment of subcritical water using Ru-containing magnetically recoverable catalysts based on magnetic silica. Three Ru-Fe_3O_4-SiO_2 samples have been synthesized using thermal decomposition of $Ru(acac)_3$, whose amounts were varied to allow for 1, 3, and 5 wt. % of Ru by loading.

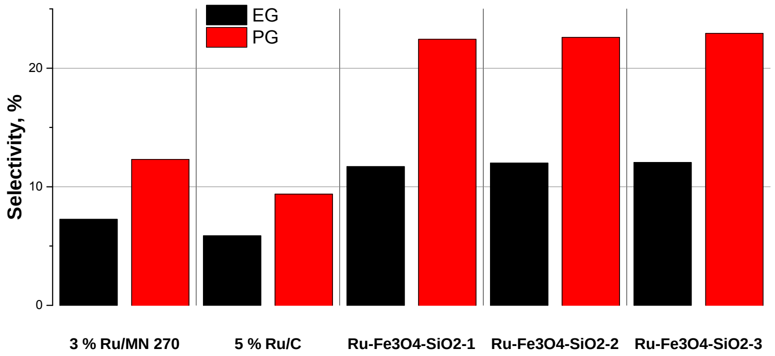

Figure 1. Selectivities to EG and PG in cellulose hydrogenolysis for the catalysts studied (0.1167 mmol Ru per 1 g of cellulose; 0.3 g of cellulose; 30 mL H_2O; 255 °C; $P(H_2)$ 60 bar)

Figure 1 shows that selectivities to EG and PG are nearly identical for all thee magnetic catalysts and much higher than those for 5 wt. % Ru/C and 3 wt. % Ru/MN 270.

It is noteworthy that cellulose hydrogenolysis with a heterogeneous catalyst is challenging considering that two solids are present in the reaction medium: cellulose and catalyst. Thus, a small amount of the catalyst is beneficial (especially for a magnetic separation) leading us to conclude that Ru-Fe_3O_4-SiO_2-3 with the highest Ru content is the most promising for this reaction because less catalyst is needed. Therefore, all further studies were carried out for Ru-Fe_3O_4-SiO_2-3. The highest selectivities to EG (19 %) and PG (20 %) were obtained for 50 min at 255 °C, 60 bar hydrogen pressure, 0.1167 mmol of Ru per 1 g of cellulose and 0.195 mole of $Ca(OH)_2$ per 1 mole of cellulose. In these conditions the cellulose conversion was 100 %. Comparing the catalytic performance of Ru-Fe_3O_4-SiO_2-3 with that of Ru/SiO_2 (containing 5 wt. % of Ru and prepared in analogous conditions), we proposed and validated a hypothesis that the Fe_3O_4 promotes hydrogenolysis.

We developed magnetically recoverable catalysts containing 2 nm Ru NPs in mesoporous Fe_3O_4-SiO_2 with the Ru nominal loading of 1, 3, and 5 wt. %. XPS showed that the surface of Ru NPs contains an equimolar ratio of Ru^0 and Ru^{4+} species. All three catalysts exhibited excellent activities in cellulose hydrogenolysis to EG and PG, independent of the Ru loading, revealing that for all three compositions the Ru NP surface is accessible to reagents. The EG and PG selectivities were shown to depend on temperature, reaction time, and Ru and $Ca(OH)_2$ loadings. It is worth noting that the activities and selectivities of the Ru-Fe_3O_4-SiO_2 catalysts described in this work significantly exceed those for the commercial Ru/C catalyst and Ru/MN-270 reported by some of us previously. These factors and the excellent stability of the Ru-Fe_3O_4-SiO_2-3 catalyst in the repeated use after magnetic recovery make this catalyst promising for industrial applications in biomass processing to value-added chemicals and biofuels.

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OXIDATIVE CONVERSION OF LIGHT ALKANES TO NEW COMPOSITE MATERIALS

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Oxidative conversion of light alkanes by air to hydrogen at T = 623-873 К and space velocity 330-15000 $ч^{-1}$ on polyoxide catalysts containing 1-, 5-,10 % Mo, Ga, Cr of different composition and ratio supported on natural Torgai clays (TC), Sary-Ozek, Chankanai, IK-30 and IR-301 zeolites. The purpose of this work is the development of new composite materials, supported on Torgai clays for the process of oxidative conversion of light alkanes tohydrogen, investigation the influence of technological reaction parameters (temperature, composition and content of catalyst active phase, contact time and composition of reaction mixture) on yield and selectivity of process, determination of optimal reaction conditions and physical and chemical properties of catalysts. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. Analysis of the reactants and products was carried out chromatographically with an “Agilent Technologies 6890N” instrument. The catalysts were investigated by X-ray diffraction (XRD), electronic microscopy (EM), infra-red spectroscopy, and their surface area, porosity, and elemental composition were determined. The investigation on influence of the nature of carrier on yield of hydrogen from reaction temperature was carried out. It was shown that more high yields of hydrogen were produced over Torgai white clay (TWC). Mo, Cr and Ga samples show more optimal properties during investigation of the series of monometallic supported over TWC catalysts. It was carried out the investigation of the physical-chemical properties of catalysts by complex methods and determined the correlation between catalytic and physical-chemical properties. The results indicate that there are reserves for increase of yield of hydrogen for granulated catalysts on a base of polyoxometallates.

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PP-18

OXIDATION OF GLYCEROL USING GOLD NANOPARTICLES ENCAPSULATED WITH CARBON AS CATALYST

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Gold nanoparticles have been an important option as catalyst to glycerol transformation to chemical inputs derived from their oxidation [1]. There are several types of gold nanocatalysts (nanoparticle size and shape; nature of the support etc.), and their choice has an important influence in the performance of the catalytic system [2]. In this work we used gold nanoparticles coated by hollow carbon spheres Au@C [3] in order to be used as catalysts in glycerol oxidation reactions. All steps of the catalyst synthesis were characterized by Electron Transmission Electron Microscopy (Figure 1).

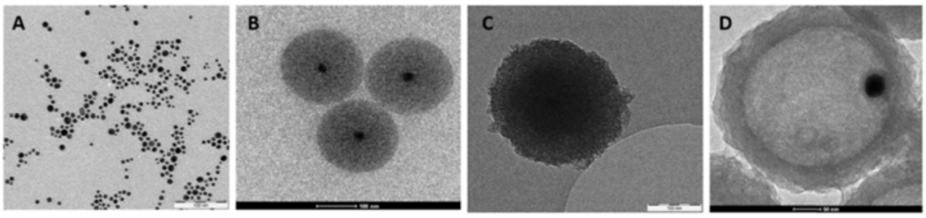

Figure 1. MET images of the nanoparticles obtained at different stages of synthesis: A) AuNP PVP; B) $AuNP_{PVP}@SiO_2$; C) $AuNP_{PVP}@SiO_2@SiO_{2m}$; and D) Au@C

From the MET image of Figure 1D, it is possible to verify that the gold nanoparticle is inside an amorphous charcoal shell. In terms of dimensions, the nanoparticles have a diameter of ca. 300 nm, the AuNP ca. 10 nm and the thickness of the bark is ca. 40 nm. The catalytic material was also characterized by TGA and Raman Spectroscopy.

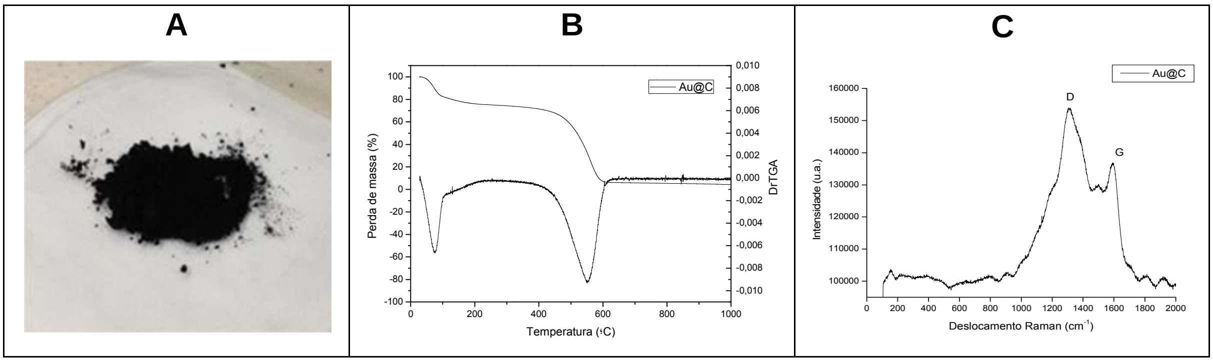

Figure 2. A) Visual appearance; B) the TGA curve; and C) the Raman spectrum of Au@C

The visual aspect of the final product is typical of a carbonaceous material (Figure 2A). From TGA (Figure 2B), it is possible to observe that the material presents a remarkable loss of mass around 450 °C, referring to elimination (burning) of the coal shell. By Raman spectroscopy (Figure 2C), two characteristic bands of compounds containing carbon, D and G bands are identified [4]. The evaluation of the catalytic activity of the system is being summarized in Table 1.

Table 1. Oxidation reactions of glycerol employing Au@C as catalyst

T (°C)	Conversion (%)[a]	Selectivity (%)[b]						
		AM	AT	AG	GA	AF	AL	AC
80	76	33	14	29	3	20	0	0
100	94	0	6	33	18	41	0	2

[a] 200 mL steel reactor; Reaction time: 3 h; Pressure: 5 bar (1 load); Mole ratio NaOH: glycerol: Au: 3000: 1000: 1.
[b] AM= mesoxalic acid; AT= tartronic acid; AG= glyceric acid; GA= glyceraldehyde; AF= formic acid; AL= lactic acid; AC= acetic acid.

The synthesis of the Au@C nanocatalyst was quite reproducible. It is possible to verify the effective reactivity of the catalyst. At the temperature of 100 °C in the used condition, there is great formation of formic acid, which indicates that reactions with breakage of the C-C bond occur. More test are in course to improve the selectivity of the system.

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CAPES, CNPq, FINEP, FAPEAL, INCT-Catálise.

PP-19

PREPARATION OF NANOCATALYSTS IN A POROUS Al_2O_3 MATRIX

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Wide-porosity carriers with a bimodal size distribution for the analyzed catalysts of oil refining technologies. The effectiveness of the method of molecular layering of TiO_2 from the vapor phase for the production of alumina and alumocaoline carriers modified with titanium dioxide is considered. Transition metals of groups VI and VIII The periodic system on carriers with a typical pore distribution: 50 nm was applied either by sequential impregnation or from the joint content of the corresponding salts. An attempt has also been made to apply molybdenum by magnetron sputtering and physical deposition.

Especially for the preparation of nanocatalysts, a monoporous Al_2O_3 matrix was used with dimensions of about 50 nm and 50 μm thick, prepared by electrochemical anodizing of aluminum foil. The peculiarities of the molecular structure of monoporous Al_2O_3 made it possible to effectively apply the molecular layering method to their solutions. For example, a porous alumina plate was immersed in an aqueous solution of $Ni\ (NO_3)\ _2\ 6H_2O$, after the first adsorption cycle of the sample, it was abundantly washed with distilled water to remove physically adsorbed nickel nitrate, dried and again immersed in the impregnating solution. After several cycles, the plate was annealed in air. Scanning electron microscopy has shown the formation of a network structure with dimensions of NiO ~ 100 nanometers on the surface and in the pores of the matrix.

The influence of synthesizer and catalyst technologies on the dispersity of transition metal particles, as well as their activity in model hydrogenation reactions of hexene-1, cyclohexene and thiophene, is compared.

SYNTHESIS OF DIMETHYL CARBONATE BY TRANSESTERIFICATION OF CYCLIC CARBONATE WITH METHANOL USING SOLID BASE CATALYSTS

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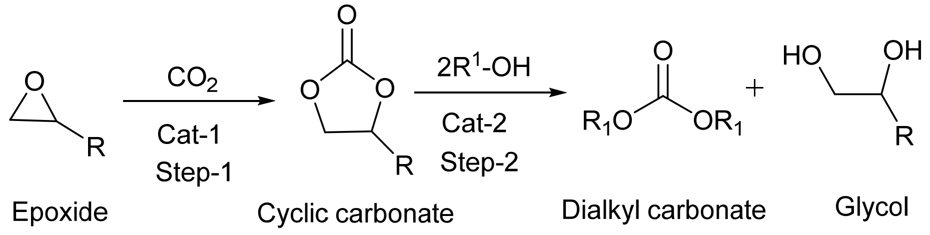
The catalytic transformation of cheap and renewable CO_2 to chemicals and fuels is highly attractive. In particular, the chemical fixation of CO_2 into cyclic carbonates and further its conversion to dialkyl carbonates via tranesterification has attracted extensive attention in both academia and industry (Scheme 1).[1] The first step (synthesis of cyclic carbonates (EC/PC)) has already been established with conversion and selectivity close to 100 %.[2] Therefore, much attention has been paid on the transesterification of cyclic carbonate and alcohol to corresponding dialkyl carbonate (eg.DMC and DEC). Dimethyl carbonate (DMC) has been proposed as a green reagent to replace highly toxic phosgene for alkylation and carbonylation reactions [3]. Worldwide consumption of DMC has been increasing continually because of its applications in fuel technology, pharmaceuticals and electrochemical, and catalytic reactions [4].



R= H OR CH_3

R^1= CH_3, CH_3-CH_2, CH_3-CH_2-CH_2 or CH_3-CH_2-CH_2-CH_2-CH_2 etc.

Scheme 1. Two step synthesis of dialkyl carbonate

Synthesis of dimethyl carbonate (DMC) by transesterification of cyclic carbonate (EC and PC) with methanol was investigated using hydrotalcites (HTs) and mixed metal oxides (MMOs) as catalysts. A series of HTs and MMOs were synthesized by co-precipitation method. All synthesized catalysts were characterized by XRD, FT-IR, TEM, N_2 sorption, benzoic acid titration and CO_2-TPD in detail and evaluated for selective synthesis of dimethyl carbonate by transesterification of a cyclic carbonate with methanol. Good results were obtained with Mg: Fe: Ce HT and Li-Al MMO as catalysts (Table 1). Among this Li-Al MMO, showed the best activity towards DMC synthesis. Activity was strongly dependent on the physicochemical properties of synthesized catalysts. Detailed optimization study was carried out for both the catalysts and catalysts were stable for 5-7 recycles maintaining high activity and selectivity towards DMC. Interestingly Li-Al MMO was found to be good catalyst for tranesterification of PC and methanol. The obtained results were found to be better than the reported heterogeneous base catalyst for this reaction.

Table 1. Transesterification of cyclic carbonate with methanol

Sr.no	Catalyst	Reaction time (h)	EC conversion (%)	DMC selectivity (%)
1	Mg:Fe:Ce (3:0.85:0.15) HT	3	87	100
2	Li-Al (MMO)	1	84	100
3	Li-Al (MMO)	3	75*	100

***** *propylene carbonate*

Reaction conditions: EC/PC: MeOH molar ratio: 1:10, Catalyst: 2.5 wt % relative to EC/PC, Reaction Time: 1-3 h, Temperature: 70 °C.

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CATALYTIC PROCESSES OF CARBOXYLIC ACIDS PRODUCTIONS FROM THE RENEWABLE RAW MATERIALS

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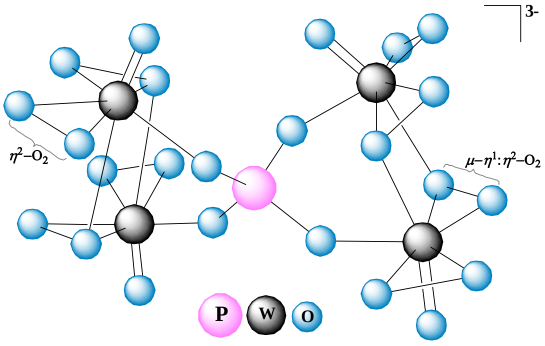
Conversion of hydrocarbons into oxygen-containing derivatives is the great interest for both basic researches and industrial purposes. In this regard the development of effective and selective catalysts for the unsaturated hydrocarbons oxidations under mild conditions is currently important [1].

The phase-transfer catalysis allows the oxidation reactions of various organic substrates to be carried out under mild conditions – at low temperature (up to 100 °C) and atmospheric pressure. The important advantage of this catalytic method is the possibility of process implementation in the absence of hazardous organic solvents. Therefore, the phase-transfer catalytic reactions can be related to the "green" chemistry. The problem of a homogeneous catalyst separation from the reaction mixture in this case is solved by separating the phases since the catalyst and the final product are in different phases – organic and aqueous, respectively.

The available and environmentally friendly 30% aqueous hydrogen peroxide is used as an oxidant. The reaction is performed in the presence of bifunctional catalytic systems based on peroxocomplexes of tungsten in combination with quaternary ammonium cations – $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q^+ is quaternary ammonium cation [2].



Schematic view of anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$

In this work it was considered of possibility of a succinic acid getting from the furfural. The last can be obtained from an acid-catalyzed hydrolysis of a pentosans-containing biomass – waste products of agricultural crops processing (sunflower, corn, etc.). Currently, the worldwide annual production of furfural is about 250-700 kt/a [3].

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As a result of the performed researches it was established that the furfural oxidation by 15 %-H_2O_2 in the presence of the catalyst $[C_5H_5NCet^n]_3\{PO_4[WO(O_2)_2]_4\}$ at 60-70 °C proceeds with the substrate conversion up to 100% but with a low yield (15-30 %). It was shown that the succinic acid yield can be increased in the presence of catalysts on the basis of the tetra(oxodiperoxotungstate)phosphate(3-) like these $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q = $[(n\text{-Hex})_4N]^+$, $[(n\text{-Bu})_4N]^+$, $[\text{Benz}(n\text{-Pr})_3N]^+$, $[\text{Me}(n\text{-Oct})_3N]^+$, by 2-2,5 times.

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FORMATION OF AROMATIC ACIDS VIA OXIDATIVE CARBONYLATION OF LIGNIN MONOMERS

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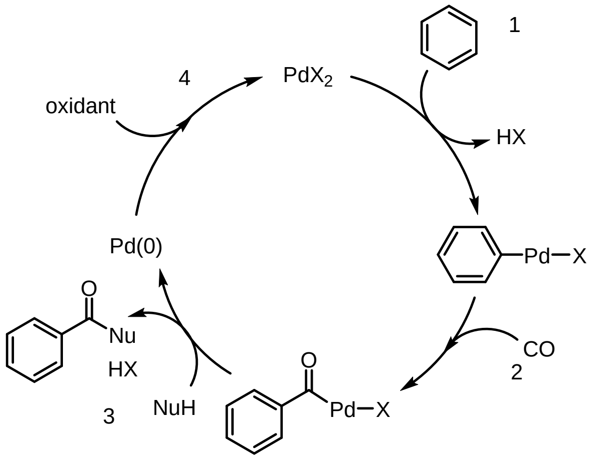
Lignin is the second most abundant natural biopolymer and due to its aromatic structure is a promising source of renewable products and chemicals [1]. The oxidation of lignin by homogeneous catalysts represents one of the most promising approaches toward the production of fine chemicals from lignin [2].The carbonylation chemistry constitutes an industrial key technology, which produces many products for our daily life. Among the different types of carbonylation reactions, palladium-catalyzed oxidative carbonylation apply various organic nucleophiles or electrophiles in presence of CO and oxidative reagents to prepare various carbonyl containing compounds [3]. Scheme 1 shows the general reaction mechanism for the direct carbonylation of arenes. In this work two lignin monomers that are produced by depolymerization of lignin at mild reaction conditions were oxidized by different reaction conditions, catalysts, oxidant aiming for high yield or aromatic acids. The best results are summarized in Table 1 and Table 2.



Scheme 1. Oxidative carbonylation mechanism of arenes

Table 1. Oxidative carbonylation of guaiacol (G)

React.	Oxidant	Catalyst	Solvent	PCO (bar)	Temp.(°C)	Yield VA* (%)	Yield MSA* (%)	Conv (%)
G	$K_2S_2O_8$*	$Pd(OAc)_2$*	TFA*	1	R.T.	46	5	100
G	$K_2S_2O_8$*	$Pd(OAc)_2$*	TFA*	1	50	36	5	86
G	$K_2S_2O_8$*	$Pd(OAc)_2$*	TFA*	1	100	30	4	97

$K_2S_2O_8$*: potassium persulfate, $Pd(OAc)_2$*: palladium (II) acetate TFA*: trifluoroacetic acid; VA*: vanillic acid;MSA*: 3-methoxysyringic acid

Table 2. Oxidative carbonylation of syringol (S)

React.	Oxidant	Catalyst	Solvent	Water μL	PCO (bar)	Temp. (°C)	Yield SA* (%)	Conv (%)
S	$K_2S_2O_8$	$Pd(OAc)_2$	TFA	100	1	50	54	100
S	$K_2S_2O_8$	$Pd(OAc)_2$	TFA	100	1	50	37	100

SA*: syringic acid

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PP-23

PHOTOCATALYTIC ACTIVITY OF Pd-DOPED $LaMnO_3$ SYNTHESIZED AT LOW TEMPERATURE

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An increasing number of attentions have been paid on perovskite (ABO_3) structure because of their excellent performances among photocatalyst, such as the photodegradation of organic pollutants and the decomposition of water for hydrogen production [1-3]. In order to enhance the photocatalytic efficiency and meet the practical application, some attempts have been made to solve the problem by coupling with semiconductors [4], modification with noble metals [5], or controlling the shape of photocatalysts [6]. A survey of the physical and chemical properties of these catalysts reveals that characteristics of perovskites are closely related to their catalytic behaviors.

In this work, we report the synthesis of the Pd-doped $LaMnO_3$ nanoparticles (at different Pd concentrations:1 %, 2 %, 3 %) via sol–gel mehod using citric acid as a chelating agent, followed by heat treatment at 600 °C, 6 h. The influence of heat treatment on phase composition, particle size, and morphology of the obtained materials have been investigated by X-ray diffraction (XRD), thermal analysis: thermogravimetric (TG), derivative thermogravimetry (DTG), surface area analysis (BET), scanning/transmission electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

The structural characterization by X-ray powder diffraction revealed that obtained materials are well crystallized, the average size of the crystallites being approximately 60 nm, as confirmed by scanning electron microscopy (SEM). From the elemental analysis (EDX) it can be seen the presence of dopant (Pd), and the elements mapping has certified the homogeneous distribution of chemical elements.

The photocatalytic activity of the as-prepared samples, evaluated by the photodegradation of aqueous methyl blue will be presented. Photocatalysis experiments will be conducted using simulated sunlight as a source of radiation.

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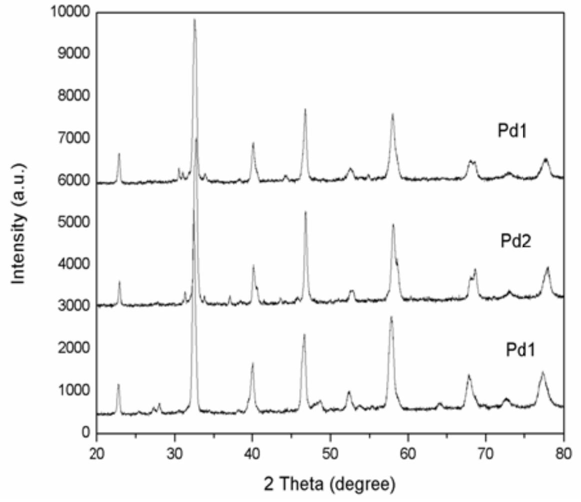
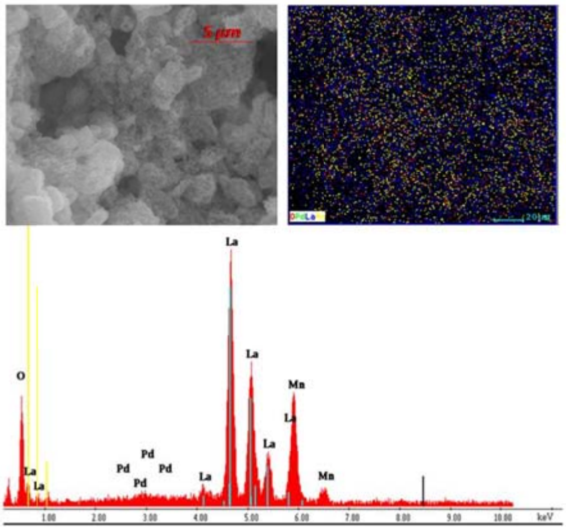


XRD patterns for Pd-doped $LaMnO_3$ annealed at 600 °C



SEM morphology, mapping and elemental analysis for $LaMnO_3$ doped 1 % Pd

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CATALYTIC PURIFICATION OF WASTE GASES FROM SULFUR IMPURITIES IN THE PRESENCE OF MODIFIED CENOSPHERES OF THERMAL POWER STATIONS

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Magnetic aluminosilicate microspheres are one of the energy ashes components from the combustion of coal in the thermal power stations furnaces, which are formed as a result of thermochemical transformations of the mineral part of coal. The combination of magnetic properties and high thermal stability makes it possible to use them as functional materials and catalysts of waste gases purification from sulfur imputities.

The microspheres phase composition is represented mainly by quartz and mullite.

The chemical composition is represented by aluminum, silicon, iron, calcium and titanium oxides (~ 95 wt. %).

IR spectra of the aluminosilicate catalyst showed that an intense absorption band is observed in the frequency range 1200-1000 cm^{-1}. This frequency range is typical for the Si–O, Al–O, Si–O–Al groups: ν – 1100, 1066, 1022, 1050, 900 cm^{-1}. The absorption bands in the low-frequency region of the spectrum from 668 to 614 cm^{-1} refer to Fe–O in the Fe_2O_3 group.

To study the kinetics of sulfur dioxide oxidation with oxygen under steady-state conditions in aqueous solutions, in the presence of modified cenospheres, Na_2SO_3 was used as a source of SO_2, since under the experimental conditions at pH 10-12 in an aqueous solution SO_2 is in the form of SO_3^{2-}:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

The main results of the microspherical catalysts study for the sodium sulfite oxidation by oxygen are summarized in Table 1.

Table 1. The sodium sulphite oxidation by oxygen in the presence of a microspherical catalyst

Exp. No.	Sample of cenospheres, g	$C_{Na_2SO_3}$, mol/l	C_{FeSO_4}, mol/l	$C_{H_2SO_4}$, mol/l	t, °C	Na_2SO_3 conversion degree, %	W_{O_2}, max, ml/min
1	0	0.4	-	-	40.0	100.0	0.6
2	0.1	0.4	-	-	40.0	100.0	5.4
3	0.5	0.4	-	-	40.0	100.0	4.4
4	1.0	0.4	-	-	40.0	100.0	4.0
5	2.0	0.4	-	-	40.0	100.0	3.4
6	0.1	0.2	-	-	40.0	100.0	4.8
7	0.1	0.1	-	-	40.0	100.0	3.6
8	0.1	0.2	$1\cdot10^{-4}$	-	40.0	100.0	4.0
9	0.1	0.2	$0.5\cdot10^{-5}$	-	40.0	100.0	4.6
10	0.1	0.2	$1\cdot10^{-5}$	-	40.0	100.0	6.8
11	0.1	0.2	10^{-2}	-	40.0	79.0	3.8
12	0.1	0.2	-	-	40.0	100.0	4.8
13	0.1	0.2	-	$1.75\cdot10^{-2}$	40.0	100.0	5.2
14	0.1	0.2	-	$5.2\cdot10^{-2}$	40.0	100.0	3.8
15	0.1	0.2	-	$8.75\cdot10^{-2}$	40.0	100.0	3.0
16	1.0	0.8	2.0	-	30.0	88.0	0.2
17	1.0	0.7	3.0	-	30.0	80.0	0.4
18	1.0	0.8	2.0	-	60.0	50.0	0.2

The table results indicate that the conversion degree and the process rate depend on the concentrations of the Na_2SO_3–Al–O–Si–Fe–H_2SO_4–H_2O system components. Under optimal conditions, the Na_2SO_3 conversion degree reaches 100 % and the maximum oxygen absorption rate reaches 6.8 ml/min. In most cases, the dependence of the Na_2SO_3 oxidation rate on the initial concentrations of components is extreme character.

PP-25

CATALYTIC HYDROGENATION OF D-XYLOSE TO D-XYLITOL: TEMPERATURE FACTOR

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Xylitol is polyol with sweet taste and well soluble in water. It is stable at high temperature, more sweetly than saccharine and does not caramelize. Thus xylitos is widely used as sweetener, as a component of tooth paste, in food, cosmetic and pharmaceutical industry as well as to produce synthetic resins [1].

In D-xylose hydrogenation two factors have great importance – temperature and pressure. High pressure is necessary to increase hydrogen solubility in liquid reaction medium. Process temperature, in turn, affects both hydrogen solubility and hydrogenation rate [2].

In [3] the authors used steel batch autoclave reactor obtain xylitol. Active metals Ru and Ni based on different supports were used as catalysts. In the presence of Ni catalyst at partial hydrogen pressure 0.1 MPa and temperature 140 °C xylitol yield does not exceed 30 %. As compared to Ni catalyst, xylitol yield in the presence of Ru catalyst reached up to 98-99 % at the same conditions.

In current work xylose hydrogenation to xylitol was carried out in the presence of Ru/MN 100 catalyst (prepared by impregnation of hypercrosslinked polystyrene MN-100 with ruthenium (IV) hydroxochloride solution in complex solvent methanol-tetrahydrofurane-water) varying reaction temperature in the range of 403-433 K. Experiments were performed at the following conditions: catalyst mass – 0.4 g; xylose initial concentration – 0.4 mol/L; hydrogen partial pressure – 4.0 MPa. It was found that the increase in temperature led to the increase in substrate conversion (Fig. 1).

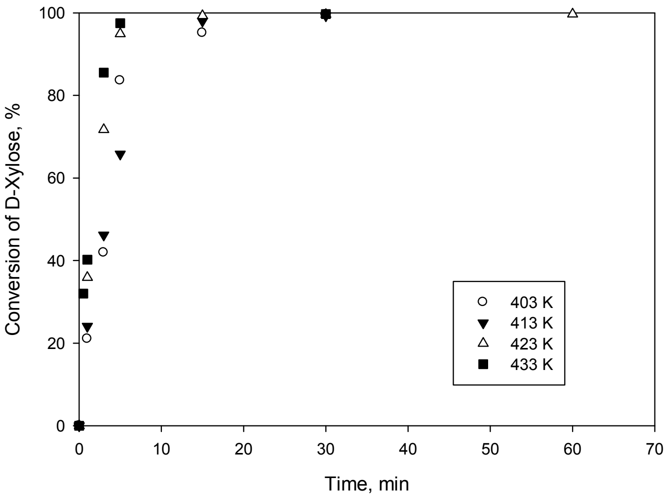

Figure 1. Substrate conversion dependence on temperature

However temperature increase negatively affects the process selectivity. Temperature growth leads to the decrease in xylitol selectivity down to 70 % at high conversion degree. It can be explained by the increase in side reactions rate as well as substrate and product decomposition at higher temperatures.

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PP-26

EFFECTS OF Ni-M_2O_3 (M: Cr, Mn, Fe) CATALYSTS ON POM PARAMETERS IN MEMBRANE REACTOR

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Application of mixed, oxygen ion and electron conducting oxides (MIECs) as ceramic membranes is promising for hydrogen production in the reactors for partial oxidation of methane (POM). Although conventional process for hydrogen production is steam reforming of methane, membrane POM reactors attract attention due to the integration of oxygen separation and methane conversion to syngas. To date, Ni catalysts for POM reactors have been widely studied because of their low cost and high activity. However, Ni catalysts tend to lose activity as a result of soot and coke formation. The additions of Cr, Mn and Fe to Ni / Al_2O_3 catalysts have been reported to improve stability Ni catalysts decreasing coke formation [1,2]. Therefore, we investigated the effects of Ni / M_2O_3 (M: Cr, Mn, Fe) catalysts on parameters of the POM prosess in the membrane reactor.

Ni-M_2O_3 (M: Cr, Mn, Fe) catalysts were synthesized by co-impregnation of commercial γ-Al_2O_3 support. The BET surface area was determined with helping Micromeritics Gemini VII analyzer. The catalytic tests were carried out in a fixed-bed flow reactor operated at atmospheric pressure. The outer shell of the reactor was made of a quartz tube. The ferrous oxygen separating membrane was set inside the quartz casing in between alumina tubes that served also as in- and outlet air ducts [3]. The membrane sizes were 1, 10 and 30 mm for wall thickness, diameter and length, respectively. The space between the membrane and the casing was filled with the catalyst. The methane conversion X_{CH_4} and selectivity S_{CO} for CO were calculated as:

$$X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100\ \% \qquad (1)$$

$$S_{CO} = \frac{CO^{out}}{CO^{out} + CO_2^{out}} \times 100\ \% \qquad (2)$$

$Ni-M_2O_3$ (M: Cr, Mn, Fe) catalysts exhibited stable parameters of the POM process. Syngas selectivity attained 96-98 % and methane conversion was 97-99 % for catalysts at methane flow values of 70-75 ml/min. The ratio of H_2/CO was 1,9. The after test examination of the catalyst did not reveal any significant soot deposits. The obtained results can be recommended for testing of the catalysts in isothermal water splitting and hydrogen production.

Acknowledgements

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PP-27

SYNTHESIS OF Zr^{4+} AND Bi^{3+} DOPED $NaNbO_3$ PEROVSKITE MATERIALS AND THE STUDY OF CATALYTIC ACTIVITY

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Due to its potential applications to many environmental pollution problems, photocatalytic degradation of organic pollutants in waste water over semiconductor perovskites materials has attracted much attention [1]. These ABO_3 type compounds have attracted great interest for the unique structural features, such as variety of structural phase transitions and the variable composition [2].

In this study, we report the hydrothermal synthesis of undoped and Zr and Bi doped $NaNbO_3$ powders with perovskite structure. This method reveals that can be obtained nanocrystalline materials with desired size and morphology at low temperatures. The obtained powders were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and the catalytic activity was studied.

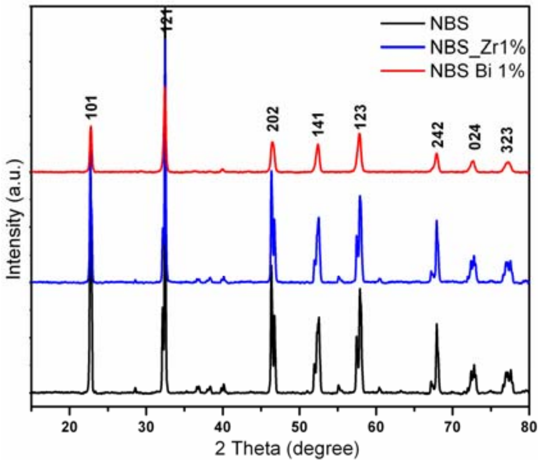

Figure 1. X-ray Difractograms for Zr^{4+} and Bi^{3+} doped $NaNbO_3$

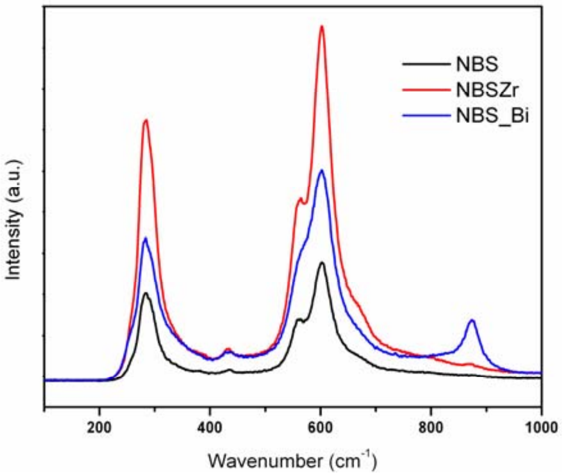

Figure 2. Raman spectroscopy for Zr^{4+} and Bi^{3+} doped $NaNbO_3$

The XRD patterns of the obtained powders by hydrothermal method at 200 °C, for 12 h are shown in Fig.1. The X-ray diffraction data indicate that all samples have the orthorhombic crystal structure with space group Pmc21.

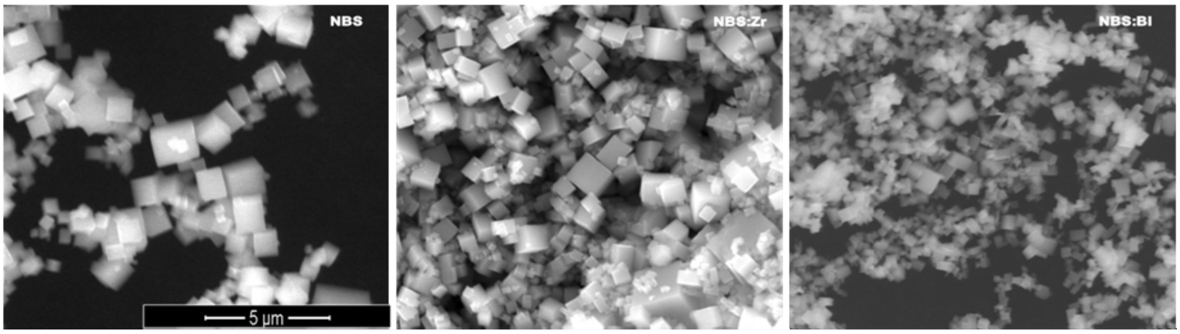

Figure 3. Scanning electron microscopy (SEM) images for Zr^{4+} and Bi^{3+} doped $NaNbO_3$

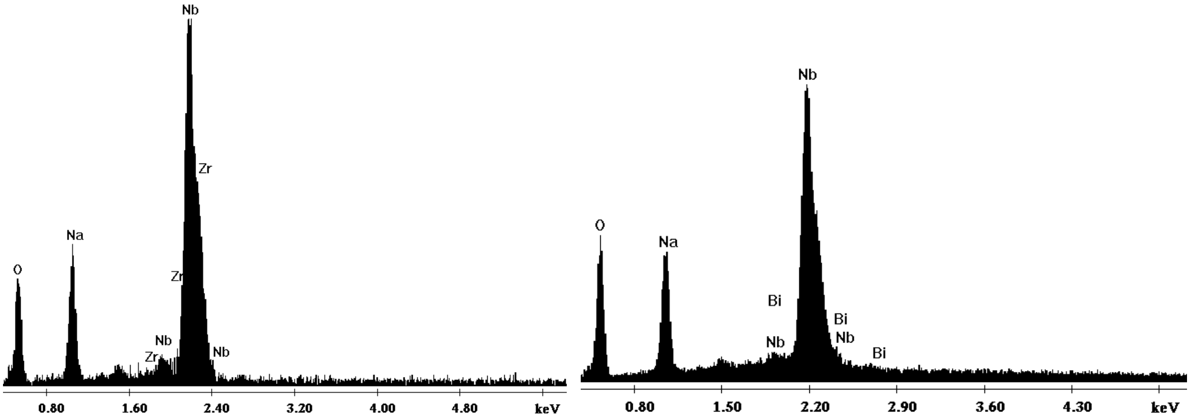

Figure 4. Energy-dispersive X-ray spectroscopy (EDX) for Zr^{4+} and Bi^{3+} doped $NaNbO_3$

From surface morphology of obtained materials it can be seen that the particles are cubic shape and well defined. The elemental analysis of the Zr and Bi doped $NaNbO_3$ samples shows the presence of Zr, respectively Bi in the $NaNbO_3$ samples.

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Acknowledgements

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PP-28

OXIDATION OF PHENOL IN THE PRESENCE OF ENZYME-LIKE CATALYSTS IMMOBILIZED ON MAGNETIC NANOPARTICLES

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We found that immobilized on a natural polymer – humic acid (HA) – $CoFe_2O_4$ ferrospinel is an active and selective catalyst for phenol oxidation, which is not inferior in catalytic properties to enzymes. It has magnetic properties and is easily separated from the reaction medium by magnetic separation. Highly dispersed magnetic $CoFe_2O_4$ particles were obtained by chemical coprecipitation using iron and cobalt chlorides and nitrates. Humic acid was extracted from brown coal of the Kiyakty deposit (Kazakhstan) according to the standard method (GOST-9517-94).

The molecular weight of the humic acid structural cell is 1500 units. The hydrolysable part of the cell makes up 45 % of the humic acid mass and includes about 6 % amino acids, up to 25 % carbohydrates and the remnants of the fulvic acid type. Six-membered cycles are represented mainly by three- and four-substituted structures, which coincide with the identified products composition of humic acids oxidation. Six-membered cycles are connected by bridges with double bonds, which creates a fairly long and continuous coupling system.

IR spectra allow us to conclude that humic acids are coordinated with $Co(NO_3)_2$. When hydrogen ions in carboxyl groups of humic acids are replaced by cobalt (II) compounds, the characteristic vibration band of carbonyl in carboxyl groups usually disappears or is weakened (ν = 1690-1710 cm^{-1}). Simultaneously, bands corresponding to vibrations of the carboxylate ion appear in the spectra. The absorption band intensity of antisymmetric vibrations increases with the increase in the filling of humic acids functional groups with cobalt ions. The Co–O bond formation in humic acid complexes is also confirmed by absorption in the frequency range 800-500 cm^{-1}, in particular, the bands at 760-660 cm^{-1} and in the 500 cm^{-1} region, which can be attributed to the stretching vibrations of cobalt carboxyls. Thus, it has been shown that carboxyl groups of humic acids are the centers for fixing magnetic composites in the role of a macroligand.

It is revealed that $CoFe_2O_4$ nanoparticles have a spherical shape, with the particle diameter reaching 7-20 nm. There is no sharp difference between the size and shapes of nanoparticles obtained by different methods.

The $CoFe_2O_4$–HA nanocomposite hysteresis curves are recorded at 300 K and represent closed lines symmetrical with respect to the coordinate system. The curves shape proves the ferromagnetic nature of the material, which makes it possible to use it for magnetic separation.

The experimental results of the catalytic phenol oxidation are summarized in Table 1.

Table 1. Phenol oxidation in the $CoFe_2O_4$–HA–C_6H_5OH–H_2O system

$CoFe_2O_4$ concentration, mol/l	HA concentration, mol/l	Phenol concentration, mol/l	t, °C	Phenol conversion degree, %	Oxidation rate, Max, mol/l*min
$1.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.12	60	99.0	$1.0\cdot10^{-4}$
$2.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.12	60	98.0	$4.0\cdot10^{-4}$
$2.5\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.12	60	89.0	$7.0\cdot10^{-4}$
$3.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.12	60	87.0	$1.0\cdot10^{-3}$
$5.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.12	60	87.0	$1.2\cdot10^{-3}$
$5.0\cdot10^{-3}$	$2.0\cdot10^{-3}$	0.12	60	86.0	$6.0\cdot10^{-3}$
$5.0\cdot10^{-3}$	$1.0\cdot10^{-3}$	0.12	60	86.0	$4.0\cdot10^{-4}$
$5.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.05	60	99.0	$8.0\cdot10^{-4}$
$5.0\cdot10^{-3}$	$5.0\cdot10^{-3}$	0.15	60	84.0	$1.0\cdot10^{-3}$
$5.0\cdot10^{-3}$	$5.0\cdot10^{-3}$	0.2	60	76.0	$6.0\cdot10^{-3}$
$5.0\cdot10^{-3}$	$5.0\cdot10^{-3}$	0.05	50	72.0	$6.0\cdot10^{-3}$
$5.0\cdot10^{-3}$	$5.0\cdot10^{-3}$	0.05	40	64.0	$5.1\cdot10^{-3}$

Throughout the $CoFe_2O_4$HA range studied, the oxygen absorbed amount does not change, the degree of phenol conversion ranges from 99.0 to 87.0 %.

ONE-POT PROCESSES OF ALKYL-SUBSTITUTED ANTHRAQUINONES SYNTHESES IN THE PRESENCE OF HETEROPOLY ACID SOLUTIONS AS BIFUNCTIONAL CATALYSTS

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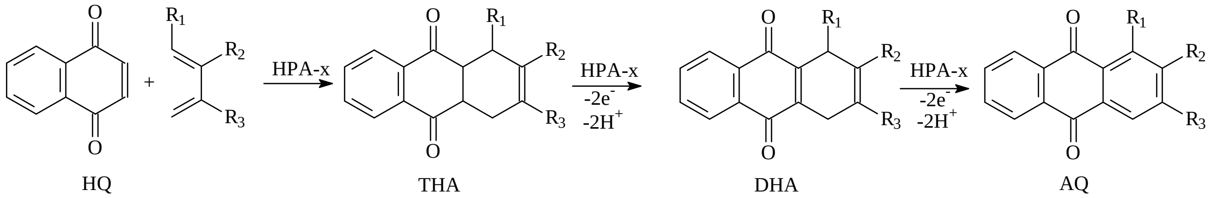
At present, anthraquinone (AQ) and its derivatives are successfully used as the catalysts in the processes of delignification of wood. A growing demand for AQ and its derivatives cannot be provided with archaic technologies of their manufacture. Acylation of benzene by phthalic anhydride according the Friedel-Krafts reaction followed by cyclization of *ortho*-benzoylbenzoic acid is the main industrial method of AQ preparation. However, in this process there is a problem of utilization of excessive acid catalyst. In another industrial process based on 1,3-butadiene reaction with 1,4-naphthoquinone (NQ), high boiling organic solvents, concentrated alkalies, and strong inorganic oxidants are used [1]. The two industrial processes produce a lot of wastes. Thus there is a problem of creating a new environmentally friendly process of AQ production.

For this purpose heteropoly acids (HPA) can be used. Now processes using aqueous solutions of Mo-V-P heteropoly acids $H_{3+x}PV^{V}_{x}Mo_{12-x}O_{40}$ are widespread [2]. Unlike many other oxidizing agents, the vanadium (V) containing HPA solutions are able to be regenerated by O_2. Thus they can catalyze the oxidation of various substrates by O_2. In the presence of HPA solutions these processes consist of two stages carried out in separate reactors **1** and **2**. In the 1st stage a substrate is oxidized by HPA. In the 2nd stage HPA is regenerated by O_2. Thus HPA solutions may be considered as *reversible oxidants*. Furthermore, aqueous HPA solutions are strong Brønsted acids and can be used as acid catalysts. Therefore, HPA solutions can be *bifunctional* (i.e. oxidative and acidic) catalysts.

We have developed new processes of substituted AQ production in the presence of high vanadium HPA solutions [3-4]. At that, we have combined *in a single technological stage* two types of reactions: 1) the acidic-catalyzed Diels-Alder reaction of 1,3-dienes with NQ giving substituted 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THA); 2) the sequential oxidation of THA by HPA with the formation of substituted 1,4-dihydro-9,10-anthtaquinone (DHA) and then substituted AQ. Thus, our *one-pot* processes are described by scheme 1.



Scheme 1. Preparation of substituted AQ in the presence of HPA solutions

Such *one-pot* processes were studied. Results are presented in the Table [3-4].

№	Substituents	Yield of substituted AQ, %	Content main product in precipitate, %
1	$R_1 = R_2 = R_3 = R_5 = R_6 = H$	67	97
2	$R_1 = R_3 = R_5 = R_6 = H$, $R_2 = CH_3$	72	98
3	$R_2 = R_3 = R_5 = R_6 = H$, $R_1 = CH_3$	91	99
4	$R_1 = R_5 = R_6 = H$, $R_2 = R_3 = CH_3$	78	98
5	$R_2 = R_3 = R_5 = R_6 = CH_3$, $R_1 = H$	70	94
Conditions: 0,2 M $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10) water solution, volume ratio HPA-10: 1,4-dioxane 1:1, reaction time 7 h, temperature 80 °C. NQ conversion ≥ 99 %.			

Our technology of the production of delignification catalysts has become more effective after we had developed a new method of the synthesis of *modified* (non-Keggin) HPA-**x’** solutions ($H_aP_zMo_yV_{x'}O_b$) [5] that are stable at elevated temperatures (160-170 °C) and can be fast regenerated by air O_2. This feature of the HPA-**x’** solutions has ensured high productivity of the processes depicted in the Scheme 1.

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VIRTUAL PRESENTATIONS

STUDY OF CATALYTIC ACTIVITY OF ULTRAFINE IRON POWDERS IN LIQUID HYDROCARBONS SYNTHESIS

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An increasing growth of global industry requires more and more resources. Nowadays oil is the main feedstock of chemical industry. However, its reserves will exhaust in the close future by today's rates of extraction and consumption. Concerning this, modern industry must find alternating source of feedstock. Using of gas-to-liquid (GTL) technologies based on Fischer-Tropsch synthesis is suggested as solution of this problem. The present technology is studied well in detail and proved its efficiency on examples of manufacturing in South Africa, Malaysia and Qatar [1].

The purpose of this research is study of catalytic features of ultrafine iron powders in liquid hydrocarbons synthesis and selection of optimal operating parameters for obtaining the desired makeup product.

The studied catalyst samples were derived by electric explosion of iron wire in media of CO. The present samples have large specific surface area, don't require pre-reduction and don't undergo fast deactivation [2].

All experiment were carried out on the laboratory unit operating with increased pressures (fig. 1).

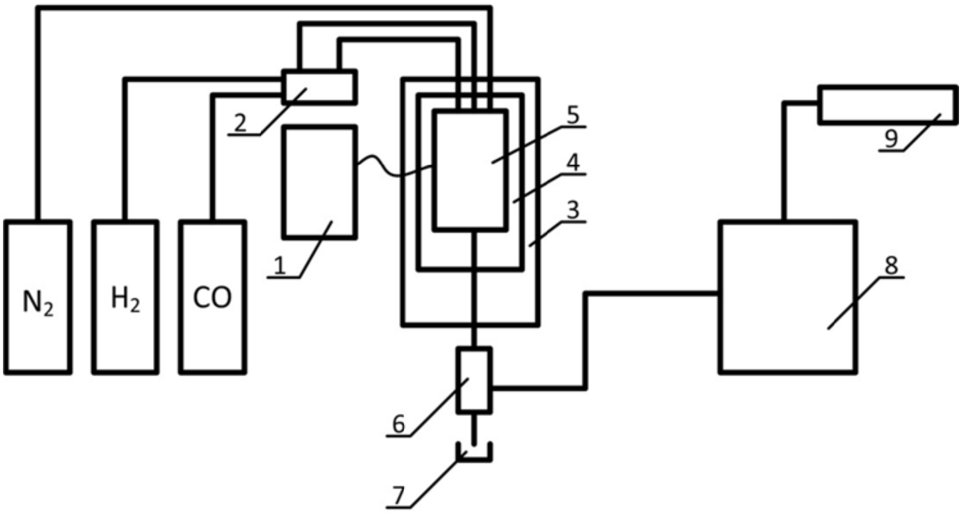

Figure 1. *The laboratory unit scheme:* 1 – temperature controller, 2 – gas metering unit, 3 – heat chamber, 4 – reactor jacket, 5 – reactor, 6 – separator, 7 – receiver, 8 – gas chromatograph, 9 – air vent

The catalyst sample was loaded into reactor, then its heating up was carried out in a flow of nitrogen, and finally reactor was fed with syngas. The H_2:CO ratio equal to 2, CO and H_2 reactants consumption 100 and 200 mln/min respectively were selected for carrying out the experiment. Pressure was 1 MPa and temperature was 250-270 °C during the synthesis. These parameters and granulometric catalyst makeup were constant while experiment was carried out.

The gases, mainly methane, are prevailing in products during the first hour of synthesis, but after 1.5 hours liquid products start to accumulate in the separator.

The liquid synthesis product contains significant amount of isoparaffins, up to 25.7 mass %, and aromatic compounds up to 27.2 mass %. Isoparaffins may be formed at the chain growth stage as result of interaction of growing chain with another hydrocarbon radicals located on catalyst active surface. Also isoparaffin formation connected with opportunity of secondary adsorption of olefins formed directly in the synthesis from CO and H_2. Readsorbing on catalyst surface unsaturated hydrocarbons izomerize on its acidic sites with formation of branched alkanes. High concentration of aromatics is caused by naphthenes dehydrogenating reaction and also unsaturated compounds cyclization reaction. Table 1 shows concentration of oxygenates in liquid products.

Table 1 – concentration of oxygenates in derived hydrocarbon mixtures

T, °C	Concentration of oxygenates, vol. %							
	Ethanol	Tert-butanol	1-propanol	Methanol	Isopropanol	Isobutanol	1-butanol	Total concentration
250	5,371	-	1,706	5,018	0,209	-	0,526	12,83
260	4,14	0,136	1,3	3,885	0,17	0,046	1,473	11,15
270	3,226	0,12	0,881	3,026	0,173	0,041	0,223	7,69

The group and phase compositions show the opportunity of using this synthesis product as a base of motor fuels and oils production.

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CATALYTIC CONVERSION OF BIOGAS TO SYNTHESIS GAS

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Extensive resources, high margin industries make biogas most promising source of hydrocarbons, capable of providing current and future needs of mankind in the energy and hydrocarbon feedstock.Biogas composition depends on the process parameters and composition of feed grade. The main components of biogas produced in anaerobic bioreactors are methane (CH_4) and carbon dioxide (CO_2), as impurities may be hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO) and oxygen (O_2). Biogas produced thus may be converted intosynthesis gas by dry reforming ($CH_4 + CO_2$), or steam reforming ($CH_4 + H_2O$) using appropriate catalysts. The relevance of this work is due to the involvement of methane and carbon dioxide - two greenhouse gases into the process of producing synthesis gas. The synthesis gas is, in turn, the raw material for a number of commercial products by industrially-applicable GTL-Technology. Thus, biogas is one of the most promising renewable fuels.

In the present work as catalysts of dry reforming of CH_4 was investigated modified nickel catalyst supported on Al_2O_3. Experiments to test the effectivity of the catalysts were carried out on an automated flow catalytic unit (PKU-1). The catalytic activity of polyoxide 4 % NiO MoO_3 / Al_2O_3 catalyst in a carbon dioxide reforming of methane was tested over a wide range of variation of the process parameters. It was defined optimal process conditions (temperature, space velocity of the reaction and the ratio of the reactants in the initial reaction mixture) for the production of synthesis gas in the carbon dioxide reforming of methane. Over the efficient 4 % $NiOMoO_3$ / Al_2O_3 catalyst at optimum process parameters ($T = 850$ °C, $W = 1000\ h^{-1}$, and CH_4: CO_2 = 1:1), the methane conversion was 98 %. Under these conditions is obtained synthesis gas with a ratio of 1:1.

VP-3

HYDROGEN PRODUCTION BY ETHANOL CONVERSION

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Bioethanol from biomass is renewable raw materials for getting valuable chemical products. The valuable products as ethylene, aromatic hydrocarbons, syn-gas, hydrogen and other products may be prepared by catalytic method from bio - ethanol. Hydrogen production from bio - ethanol provides significant environmental benefits since the resulted CO_2 is consumed again for biomass growth.

In this paper we present the results obtained in hydrogen production by conversion of ethanol using oxide supported copper catalysts modified by Cr_2O_3, ZnO and CeO_2. The catalysts were prepared by wet impregnation of the support with an aqueous solution of copper nitrate. Experiments to test the efficiency of the catalysts were carried out using an automated flow catalytic device. The reaction was performed at atmospheric pressure and the temperature was studied in the range of 200-400 °C.

The results showed that the oxide catalysts CuO, ZnO, Cr_2O_3, and CeO_2 supported on γ-Al_2O_3 have been studied during the conversion of bioethanol to hydrogen. The optimal catalyst for the production of hydrogen is 3% CuO / γ-Al_2O_3 (20 % H_2). Modification of 3% CuO / γ-Al_2O_3 with chromium oxide or zinc oxide helps increase the hydrogen yield to 46-48 vol. % at 300 °C and a space velocity of 1 h^{-1}. Based on the results of electron microscopy, the presence of nanoparticles with dimensions of 2-5 nm is observed on the investigated catalysts. The modification of catalysts with ZnO or Cr_2O_3 leads to an increase in the dispersion of the catalyst, which contributes to an increase in the activity of the catalyst in the direction of hydrogen production.

PRODUCTION OF CHEMICALLY PURE HYDROGEN BY THE HYDROGENATION-DEHYDROGENATION REACTIONS OF AROMATIC COMPOUNDS

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Chemically pure hydrogen is essential for use in fuel cells to generate electricity. Hydrogen produced from renewable raw materials biotechnologically contains a lot of impurities which deactivate the fuel cell batteries. Therefore, the effective development of hydrogen energy is need hydrogen accumulation systems, safe storage and preparation of chemically-pure hydrogen.

Hydrogenation of benzene was carried out in a laboratory high pressure autoclave PARR-300 by stirring the reaction mass at a temperature of 180 °C and pressure 70 atm and naphtalene at 280 °C and 90 atm. We have used hydrogen produced from renewable raw material to hydrogenation of benzene and naphtalene. Dehydrogenation of cyclohexane and decalin [1] prepared by hydrogenation was carried out at temperatures 260-340 °C and flow rates 1 h^{-1} in a flow reactor. The activities of various catalysts based Pt, Pd and Ni in reversible reactions of hydrogenation-dehydrogenation of aromatic compounds have been compared in order to produced chemically pure hydrogen from hydrogen-containing mixture. Hydrogen purity from dehydrogenation reactions was checked by chromatography.

As a result, the possibility of selective accumulation and generation of chemically pure hydrogen instead of hydrogen from renewable raw material is shown [2].

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VP-5

A STUDY OF THE CATALYTIC PROPERTIES OF COMPOSITE OXIDE MATERIALS OBTAINED BY TRANSIENT ELECTROLYSIS

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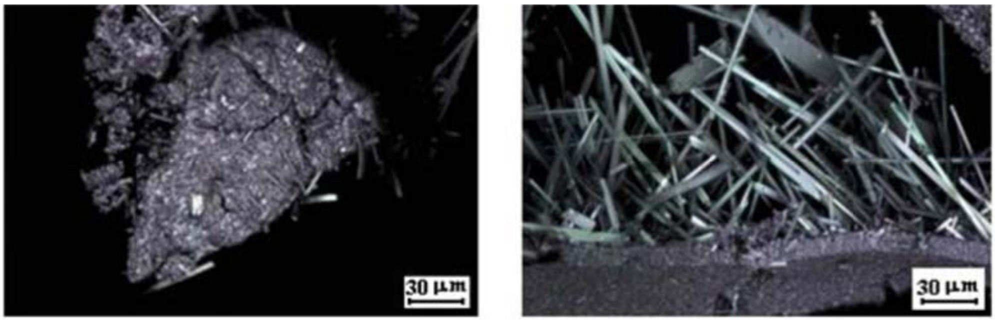
The development of composite materials on the solid support based on transition metal oxides, including molybdenum oxide compounds with a wide range of practical application [1-3] is a promising trend of surface modification. Composite coatings based on molybdenum oxides are especially attractive because of their atypical chemistry resulting from multiple valence states. In addition, they are stable, have significant activity and selectivity in different processes.

In the present work composite materials based on molybdenum, cobalt, nickel, and iron oxides deposited on a steel surface from aqueous solutions of their salts upon polarization by alternating asymmetric current were obtained. The device consisting of two paralleled diodes conducting a current in different directions through the adjustable resistance was used as a technological current source. The main electrolyte aqueous solution components were iron(II) sulfate ($FeSO_4 \cdot 7H_2O$), cobalt sulfate ($CoSO_4 \cdot 7H_2O$), ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, nickel sulfate ($NiSO_4 \cdot 7H_2O$), boric ($H_3BO_3$) and citric ($C_6H_8O_7$) acids. The asymmetry parameter (j_k:j_a) was equal to 1.44; the electrolyte temperature 65-70 °C; pH – 4; and coating deposition time – 60 min.

The phase composition of the composite oxide coatings was studied with the ARL X'tra diffractometer, with the coating substance in the form of dispersed powders produced by deposition of coatings on a technical titanium VT1-0 foil and their easy removal because of the exceedingly low adhesion. The disperse powders of the coating substance were also used in analyses with KEYENCE VK-9700 Generation II color 3D laser scanning microscope.

The X ray diffraction data demonstrated that the phase composition of the coating substance is rather complex. The basic phases of the coating composition are molybdenum oxides (MoO_3, MoO_2, and $Mo_{18}O_{52}$), spinel (Fe_3O_4), and cobalt, nickel, and iron molybdates ($CoMoO_4$, $NiMoO_4$, and $FeMoO_4$).

The electron-microscopic study of oxide compounds obtained demonstrated that these compounds are present in coating composition in the form of agglomerates of particles (Fig. 1a) having a needle morphology (Fig. 1b).



a b

Fig. 1. Micrographs of the composite coatings substance.
(a) Agglomerates of oxide compounds and (b) structure of separate particles

Developed composite oxide materials were investigated for their potential use as catalysts in liquidphase oxidations of glyoxal to glyoxylic acid. The test results showed that their catalytic activity is greater than that of existing analogues: the conversion value is higher by 13 %, and the selectivity value by 20 %. Composite coatings based on transition metal oxides not only have good catalytic properties, but good performance characteristics as well. Corrosion protective properties increase by 25 to 50 fold when the coating thickness is 15 microns.

The real advantage of the above research is the fact that for the first time, composite materials based on molybdenum oxides, complex molybdenum oxides and its oxygen compounds with iron group metals were obtained on a solid substrate by deposition of their salts from aqueous solutions using transient electrolysis.

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VP-6

CARBON DIOXIDE HYDROGENATION OVER Fe/K/C AND Fe-Cu/K/C CATALYSTS UNDER SUPERCRITICAL CONDITIONS

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The problem of carbon dioxide utilization can be solved by converting of this greenhouse gas into intermediates that can be further transformed into high value-added products. The first option of CO_2 utilization is hydrogenation reaction. The primary products of CO_2 hydrogenation are carbon monoxide, methane (synthetic natural gas) and methanol – the key intermediates that can be further transformed by present technologies [1, 2]. Whereas the catalytic conversion of CO_2 into CO, methanol and hydrocarbons is well-known, the use of supercritical $scCO_2$ in these reactions was in the focus of only a few recent publications [3-6].

The present study is devoted to the CO_2 hydrogenation under supercritical CO_2 conditions on Fe/K/C and Fe-Cu/K/C catalysts (20 % Fe, 1 % Cu and 0.8 % K). Commercially available Sibunite (synthetic porous carbon-carbon composite material) was used as a support for catalysts preparation by wetness impregnation technique. The reaction of CO_2 with H_2 (H_2:CO_2 ratio 1:1) was studied under supercritical conditions (at 523-673 K and 8.5 MPa) in a flow type reactor. Analysis of products was performed with a gas chromatograph with a thermal conductivity detector and Porapack Q and zeolite CaA packed columns.

The interaction of CO_2 and H_2 on both catalysts results mainly in the formation of CO by the reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). The selectivity to CO was more than 50 %. Other products were C_1-C_{14} hydrocarbons (mainly CH_4) witch forms apparently by further conversion CO and H_2 (Fischer–Tropsch process). The Cu-containing Fe-Cu/K/C catalyst was more active and selective to hydrocarbons in comparison with Fe/K/C. The studied catalysts exhibited a rather good stability at experimental conditions. The main advantage of the process under supercritical conditions is the enhancement of the productivity due to the use of the high-density media.

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VP-7

ISOBUTANE ALKYLATION WITH ISOBUTENE ON SOLID ACID MoO_3/ZrO_2 CATALYSTS

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A promising direction in the development of alkylation processes is the transition from a liquid-phase catalysts such as HF and H_2SO_4 to a heterogeneous catalysis thus avoiding problems related to chemical corrosion of equipment, toxicity of waste acids and their disposal. For this purpose, catalysts based on sulfated oxides of Zr, Al, Si, Ti, Sn can be used, particularly sulfated zirconia (SZr) and alumina-zirconia (AlSZr) compositions featuring high activity in alkylation. However, the main problem of a wide application of SZr and AlSZr-catalysts is their relatively fast deactivation in the course of alkylation, which is most often associated with side reactions: formation of high molecular hydrocarbons which block the pore structure and the surface active sites. Therefore, now are relevant alternative strong solid acid catalysts, for example, WO_3/ZrO_2 [2] or MoO_3/ZrO_2 systems which also have the properties of solid superacid.

In this work MoO_3/ZrO_2 catalysts are investigated which were prepared by impregnation method $ZrO_2 \cdot nH_2O$ powder of ammonia heptamolybdate aqueous solution with various wt. % MoO_3 (4.2, 6.6, 9 and 13.2%) and calcined at 600 °C for 2 h. $ZrO_2 \cdot nH_2O$ were prepared by precipitation from 10 wt. % $ZrOCl_2$ solution and 28-30 wt. % ammonia solution at pH=10, further it was filtered and washed with distilled water and dried at 100 °C 18 h.

Investigation of activity of the resulting catalysts in the process of isobutane alkylation with isobutylene performed on flow unit under the following conditions: t = 80 °C; p = 17 atm; feed rate of isobutene 1.8 ml/min. Additionally the samples were characterized by different physico-chemical methods (XRD, N_2 adsorbtion, FTIR adsorbed pyridine). The results of the analyzes and tests] shown in Tables 1 and 2 in comparison with WO_3/ZrO_2, and SO_4/ZrO_2 [2].

It was revealed change occurs as the porous structure of MoO_3/ZrO_2 catalyst and the acidic properties of the surface with increasing MoO_3 loading. All this is directly reflected in their catalytic activity (table 1). With the increase of MoO_3 loading, the volume fraction of t-ZrO_2 (V_t), SSA, quantity of Brønsted acid sites (BAS) and

BAS/(LAS+BAS) ratio is increased (table 2). Perhaps, the last observation allows to explain increase of the activity and selectivity parameters MoO_3/ZrO_2 catalysts suggesting an important role of the Brønsted acid for isobutane alkylation.

Table 1. MoO_3/ZrO_2 catalyst activity and selectivity

	4,2% MoO_3	6,6% MoO_3	9% MoO_3	13,2% MoO_3	18% WO_3 [2]	SO_4/ZrO_2 [2]
Isobutene conversion (0.5 h), %	20,0	25,1	65,8	41,2	64,1	58.0
$\sum C_5$-C_8,	94,0	89,3	86,2	96,6	91,9	94.9
C_8	29,2	56,5	68,4	58,6	80,7	79.7
2,2,4-TMP	0	0,5	11,7	0,3	29	32.6
C_{10}-C_{13}	5,5	3,3	7,1	1,3	8,1	5.0
I/O ratio	19.9	19.9	16.6	19.9	7.4	7.4

Table 2. Physicochemical properties of MoO_3/ZrO_2 catalyst

	4,2% MoO_3	6,6% MoO_3	9% MoO_3	13,2% MoO_3
SSA, m^2/g	78.3	84.6	98.2	120.1
$\rho_{Mo,\ surf}$, atoms/nm^2	2.24	3.34	3.83	4.59
V_t, % vol.	72.3	93.4	100	100
BAS/(BAS+LAS)	0.092	0.221	0.544	0.754

The received results showed that MoO_3/ZrO_2 catalysts are also promising in the alkylation of isobutane on a par with WO_3/ZrO_2 catalyst. However, further researches on influence of parameters of preparation of catalysts for the purpose of finding of optimum conditions of their preparation are necessary.

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VP-8

SYNTHESIS OF NOVEL BORON COMPLEXES BL BASED ON O DONOR ATOM LIGANDS - 2,2'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (L1)

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Boron and its derivatives are of great interest since they are used in many areas from agriculture to industry, such as glass, ceramic, textile, automotive, electronics and nuclear industry, medicine, pharmaceutical and cosmetic industry, energy, construction industry, communication tools, detergent [1,2]. Due to the widespread usage of the boron compounds, the synthesis and application of these systems in science and technology have attracted the attention of researchers in recent years.

General Procedure for Synthesis of BL

1 mmol of the ligand was dissolved in 20 mL toluene in a round bottom flask. Then the equivalent amount of the boronic derivative which approximately corresponds to 1 mmol was added, after which the ligand solution turned completely clear. The reaction mixture was maintained to stirring for 5 h at 110 °C. Different gradations of yellow colored precipitations were filtered and washed with excess of solvent. Then they were dried in a ventilated oven.

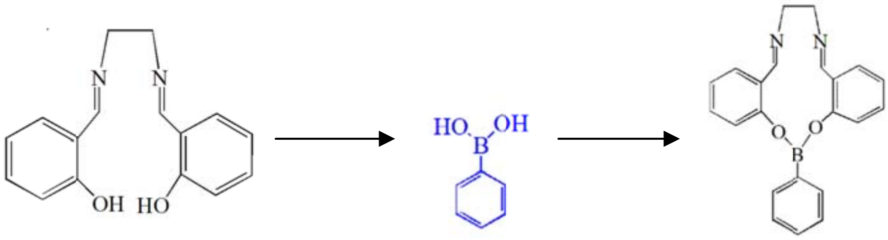
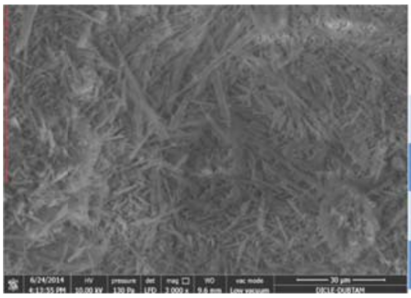


Figure 1. Reaction of Boronic Derivative with ligand

SEM and EDX Results of Compounds

Surface morphology of boron based compounds was determined under reduced pressure at different magnifications. The EDX analyses were also taken simultaneously. Qualitative elemental analyses especially for boron are very meaningful as expected. So, existence of boron supports the complexation reaction over oxygen atoms on ligand. BL have a homogenous dispersion in image. It looks like skewed fibers and single phase. However, the clearness of images for boronic complexes depends on the amorphous and crystallinity percentages and also the conductivity of the materials. If the amorphous content is more than crystallinity, the sharpness of SEM images will be excellent.



Element	Weight %	Atomic %	Net Int.
B K	10.69	12.09	14.1
C K	74.48	75.86	477.9
N K	6.48	5.66	8.1
O K	8.36	6.39	37.9

Figure 2. SEM Images and EDX Data of BL

Conclusions

We have synthesized ligands including O donor atoms and their novel kinds of boron complexes. The compounds were characterized with various techniques. They were all seen structurally convenient as expected. Obtained complexes can be implemented for conversions of aromatic ketone to corresponding alcohols. The results provide us that boron compounds are utilizable since their nature is catalytically active. That’s why it can be preferable instead of expensive catalysts like rhodium, ruthenium and iridium.

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VP-9

MULTI-PURPOSE CATALYTIC PLATFORM, BASED ON STRUCTURALLY MODIFIED TRANSIENT METAL OXIDES

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Proven catalytic technologies remain partial solution against exhaust gases of varying origin and composition. Drastically changing content and humidity shorten catalyst lifecycle inline with known catalytic poisons, products of sulphur, phosphor, carbon and nitrogen incomplete oxidation. Expenses and difficulties of catalyst utilization and/or recovery spur the community towards development of novel systems, while reassessment of known technologies may also prove useful. It has been predicted and experimentally proven, that well-known volumetric thermal expansion technology, applied to transient metal oxide compositions, provides us with structurally reinforced aggregates of artificially-stabilized phase composition and desired morphology. While traditional approach assumes composition of required metal(s) organic salt(s) being thermally exposed on air or within inert atmosphere or vacuum, to provide oxide or metal of desired purity, we added an excess of various ammonia organic salts to provide reduction atmosphere in the beginning of the thermal decomposition. Heating of the ultrafine disperse composition of above-mentioned salts at 15 Celsius degrees per minute, upto 900 °C within an hour, leads to superdiffusion among the oxide lattices involved, that results in desired polymorphic changes for dual and complex oxides within artificial dendrite being formed on their basis. Technology novelties also let us to eliminate both thermal and structural prehistory and to perform one-step synthesis of novel functional material, aimed on unattended catalytic processes. According to excessive physico-chemical analysis, including SEM, XRD, elemental, but not limited to, the technology being discussed allows the investigator to take full control over aggregates size and shape, as well to control volumetric dendrite growth, all valuable for possible product customization. Worth mentioning that XRD data of the process stages is well-described with Ginstling and Wagner diffusion models and suits them, and mathematical forecasting of the processes discussed shows promising results from the very beginning. According to rigorous lab testing, we believe that our catalytic platform stands well in many industrial processes, including CO oxidation, ammonia synthesis, automotive tunnel exhaust air treatment, pure and applied organic synthesis and many more, conversion rates shown overcome many commercial catalysts, ceria and platinum for example, being much cheaper. Despite of limited availability of many precursors (organic salts of desired transient metals), advanced co-precipitation technologies have been developed also, so the whole technology is not only ready for catalyst factory, but matches guidelines of green chemistry and technology. The only bypass product may be treated as liquid potassium fertilizer. As for gaseous byproducts of catalyst synthesis, primarily ammonia and CO, they may also be treated for production purposes in many ways, including passage over the catalyst made earlier.

Testing within many processes shows high conversion rate and high structural, phase and thermal stability, catalyst is immune to known catalytic poisons, possesses high regeneration capabilities and is able to self-clean while working, especially against soot. Catalyst structure and composition are likely to many oxide-containing minerals, so we don’t presume possible difficulties when it comes to utilization, some properties allow biodegradability, but latter requires further investigations.

One of the next steps we plan is to analyze various industrial solid wastes, especially from various electrochemical and metallurgical processes, containing many valuable metals, to perform physico-chemical analysis and to customize the mixture of organic acids, salts and the very waste to convert it to catalyst. Another pathway would lead to cheap regeneration technologies for those metals, bases on similar noveLties.

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